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Synthesis of Phosphine Trans-Substituted Derivatives of Iron Pentacarbonyl

Karl Heinz Hecker

Eastern Illinois University

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SYNTHESIS OF PHOSPHINE TRANS-SUBSTITUTED DERIVATIVES

OF IRON PENTACARBONYL
(TITLE)

BY

Karl Heinz Hecker

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1986
YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
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SYNTHESIS OF PHOSPHINE TRANS-SUBSTITUTED DERIVATIVES

OF IRON PENTACARBONYL

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To those closest to me - Mama, Josef, Ursula, Jutta,
Michael, and Wanping.

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I thank Carol Boecker for preparing some of the iron carbonyl complexes and for performing the ^{1}H NMR experiment.
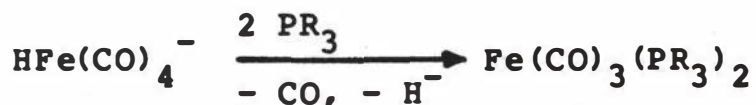
ABSTRACT

TITLE OF THESIS: Synthesis of phosphine trans-substituted
derivatives of iron pentacarbonyl

NAME: Karl Heinz Hecker

THESIS DIRECTED BY: Dr. Richard L. Keiter

The synthesis of <u>trans</u>-$Fe(CO)_3(PR_3)_2$ (PR_3 = PPh_3, PPh_2Me, PPh_2CHCH_2, $P(c-C_6H_{11})_3$, $P(n-C_4H_9)_3$, PPh_2H) can be achieved by refluxing iron pentacarbonyl under reducing conditions in the presence of ligand in 1-butanol. Addition of iron pentacarbonyl to a 1-butanol solution of sodium borohydride at room temperature results in a quantitative conversion of the iron carbonyl complex to the corresponding mononuclear formyl complex. Upon heating the initially formed formyl species decomposes to form the tetracarbonylhydridoferrate(0) anion. This hydride is believed to undergo reaction with the phosphine ligand to yield the isolated trans-substituted iron complex.

$$Fe(CO)_5 \xrightarrow[\substack{RT,\ 1\text{-butanol} \\ -\ BH_3}]{BH_4^-} (CO)_4Fe(CHO)^-$$

$$(CO)_4Fe(CHO)^- \xrightarrow[-\ CO]{heat} HFe(CO)_4^-$$

$$HFe(CO)_4^- \xrightarrow[-\ CO,\ -\ H^-]{2\ PR_3} Fe(CO)_3(PR_3)_2$$

Even though traces of monosubstituted product were detected in the crude reaction mixture by infrared spectroscopy, uncontaminated trans-substituted complexes were isolated after crystallization from dichloromethane/methanol.

All complexes have been found to be sensitive to oxygen if in solution, with the rate of decomposition depending on the kind of ligand. However, if they are dry and under vacuum no apparent decomposition takes place. All synthesized complexes have been characterized by IR spectroscopy, ^{31}P NMR, and by their melting points.

The value of the presented synthesis is based on its high selectivity, extremely short reaction time, good to very good yields, and its simplicity.

"PROOF: Evidence having a shade more of plausi-
bility than of unlikelihood."

Ambrose Bierce

"REASON: To weigh probabilities in the scales of
desire."

Ambrose Bierce

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Chapter I - Introduction

I.1 Phosphine Substituted Derivatives of Iron Pentacarbonyl

Transition metal carbonyls have been known and have been the subject of investigation for almost a century.[1] Their role in the development of coordination chemistry, in synthetic organometallic chemistry, as well as their importance as catalysts and reagents in organic synthesis and industrial processes[2] has ensured a steady interest in transition metal carbonyl complexes. The interest of the present work is focused on trans-substituted derivatives of iron pentacarbonyl, where the substituents are various monodentate tertiary phosphines. This particular kind of ligand has been chosen since it exhibits a number of advantages over other ligands.[3] The ligands in question are readily available and are of reasonable stability towards hydrolysis and sometimes oxidation. Furthermore, most tertiary phosphine ligands are of sufficient inertness towards a large number of substrates which is important if used as cocatalysts in homogeneous catalysis. Another reason for choosing phosphine ligands is their ability for stabilization of metal atoms in low oxidation states via π-back-bonding if substituted with electronegative moieties.

Phosphine derivatives of iron pentacarbonyl were first mentioned by Reppe and Schweckendiek[4] as the products of

the direct reaction between triphenylphosphine and iron pentacarbonyl. From then on many attempts have been made to prepare either mono- or disubstituted phosphine derivatives selectively. At this point a historical overview shall be provided of the methods used to synthesize $Fe(CO)_3(PR_3)_2$ complexes. In order to evaluate the described methods the following points will be considered.

1. Selectivity of the reaction

    Selectivity shall be defined as the ability to synthesize monosubstituted or disubstituted products only. This feature is important since mixtures of both complexes are difficult to separate in general.

2. Yield of the reaction

3. Reaction conditions

4. Availability of the starting materials

I.2 Previous Methods of $Fe(CO)_3(PR_3)_2$ Synthesis

2.1   Methods Based on CO Dissociation

2.1.1 Thermal Dissociation of CO

The first methods in $Fe(CO)_x(PR_3)_y$ synthesis, where x = 3, y = 2 or x = 4, y = 1, were based on CO dissociation from $Fe(CO)_5$ and subsequent substitution of the resulting 16-electron iron compound by phosphine ligands (PR_3) according to equations (1) and (2). In these reactions the dissociation of the CO ligand was caused thermally.

$$Fe(CO)_5 \xrightarrow{\text{heat}} Fe(CO)_4 + CO$$
$$Fe(CO)_4 + PR_3 \longrightarrow Fe(CO)_4PR_3$$
$$\overline{Fe(CO)_5 + PR_3 \xrightarrow{\text{heat}} Fe(CO)_4PR_3 + CO} \qquad (1)$$

$$Fe(CO)_4PR_3 \xrightarrow{\text{heat}} Fe(CO)_3PR_3 + CO$$
$$Fe(CO)_3PR_3 + PR_3 \longrightarrow Fe(CO)_3(PR_3)_2$$
$$\overline{Fe(CO)_4PR_3 + PR_3 \xrightarrow{\text{heat}} Fe(CO)_3(PR_3)_2 + CO} \qquad (2)$$
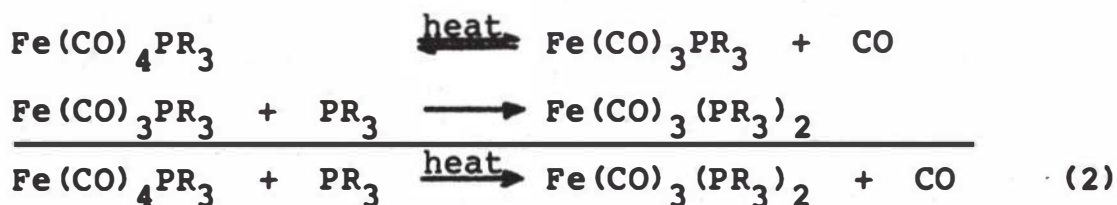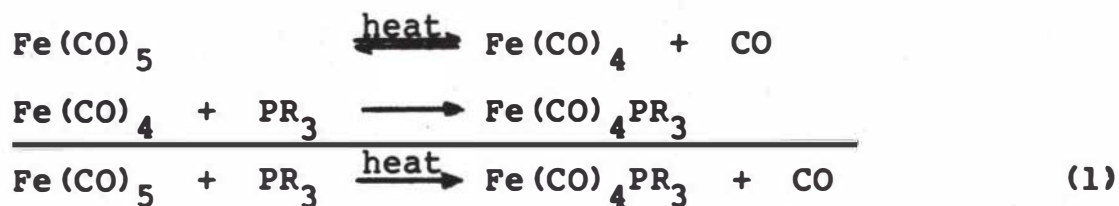
Reppe and Schwenckendiek[4] who first reported the synthesis of iron carbonyl complexes of triphenylphosphine from the direct reaction of $Fe(CO)_5$ and PPh_3 in 1948 did not give

any details. In 1960 Cotton and Parish[5] reported the synthesis of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ from the reaction of iron pentacarbonyl and triphenylphosphine in a Carius tube without solvent. After three hours at 110 $^\circ$C the precipitate formed was washed with ether, dissolved in benzene and filtered. The mono- and disubstituted products were separated by vacuum sublimation from the dried residue after evaporation of benzene. No yields were given by Cotton and Parish for the products.

Clifford and Mukherjee[6,7] prepared the triphenylphosphine derivatives from iron pentacarbonyl and PPh_3 in 1963. After a reaction time of one hour the crude reaction mixture was diluted with an equal volume of petroleum ether. Upon cooling of the solution the products precipitated from the solution and were filtered, washed with petroleum ether, and dried. Separation of the two compounds $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ by vacuum sublimation gave both products in yields of 15 % each.

In the direct reaction of $Fe(CO)_5$ with phosphine ligand in a Carius tube or in solution the yields are generally poor and mixtures of mono- and disubstituted products which are difficult to separate are obtained. However, in the early sixties it was also found by Clifford and Mukherjee[6,7] that the yield could be increased if the more expensive triirondodecacarbonyl was used. $Fe_3(CO)_{12}$ was allowed to react with PPh_3 in dioxane or THF at about 70°C for 45 minutes under nitrogen. After purification of

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the products and separation by sublimation, $Fe(CO)_4PPh_3$ was obtained in a 34 % yield and $Fe(CO)_3(PPh_3)_2$ in a 27 % yield. Even though the yields are doubled compared to the direct reaction of $Fe(CO)_5$ with PPh_3, this method still suffers from a low yield, the disadvantage of an expensive starting material, and a mixture of products that is difficult to separate.

More than twenty years later Shojaie and Atwood[8] investigated the kinetics of the reaction of the triiron cluster with different ligands. The reactions were carried out in hexane under nitrogen at 25, 30, and 35 °C with a large excess of ligand, while the kinetic data were obtained by monitoring the decrease in the absorbance at 2045 cm^{-1} due to $Fe_3(CO)_{12}$. For the ligands of interest (PPh_3, PBu_3) it was found that the reaction occurred according to equations (3) and (4).

$$Fe_3(CO)_{12} + PR_3 \xrightarrow{-CO} Fe_3(CO)_{11}PR_3 \qquad (3)$$

$$Fe_3(CO)_{11}PR_3 \xrightarrow[-CO]{+PR_3} Fe(CO)_4PR_3 + Fe(CO)_3(PR_3)_2 \quad (4)$$
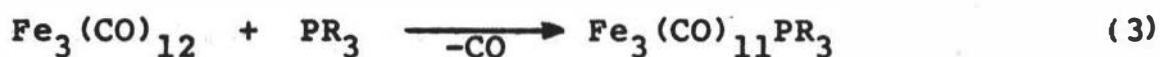
Shojaie's and Atwood's data are consistent with CO dissociation from the triiron dodecacarbonyl for the initial substitution to $Fe_3(CO)_{11}PR_3$. The course of the reaction then proceeds by fragmentation rather than further substitution in the case of PPh_3 and PBu_3 to yield the mono- and

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disubstituted compounds.

2.1.2 Photochemical Dissociation of CO

The first successful attempt to synthesize phosphine substituted derivatives of iron pentacarbonyl photochemically was undertaken by Walter Strohmeier and Franz-Josef Mueller[9] in the mid nineteen sixties. They reported the synthesis of a number of monosubstituted phosphine derivatives of $Fe(CO)_5$; however, no details were given. In 1969 the same scientists reported the photochemical preparation of mono- and disubstituted iron carbonyl compounds using iron pentacarbonyl as the starting material.[10]

Upon irradiation the mononuclear iron pentacarbonyl first reacts to give the binuclear compound $Fe_2(CO)_9$[11] according to equation (5). Further irradiation in the presence of ligand generally yields mono- and disubstituted mononuclear products as shown in equation (6).

$$2\ Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO \qquad (5)$$
$$Fe_2(CO)_9 + L \xrightarrow{h\nu} Fe(CO)_4L + Fe(CO)_3L_2 \qquad (6)$$

Strohmeier and Mueller irradiated a solution containing $Fe(CO)_5$ in a quartz vessel, while the solution was stirred and purged with nitrogen.[12] In the case of $P(c-C_6H_{11})_3$, benzene was used as a solvent. After an irra-

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diation time of 12 hours at room temperature and a number of purification and separation steps (Al_2O_3 column, high vacuum sublimation, recrystallization), the monosubstituted compound was obtained in a 46 % yield and the disubstituted product in a 35 % yield. The substitution of $Fe(CO)_5$ with $P(n-C_4H_9)_3$ was carried out in heptane using a tenfold excess of ligand. Irradiation for 24 hours and subsequent purification gave $Fe(CO)_4P(n-C_4H_9)_3$ in a 64 % yield and $Fe(CO)_3[P(n-C_4H_9)_3]_2$ in a 13 % yield.

Recently M. Therien and W. Trogler[13] selectively synthesized the disubstituted PMe_3, $P(n-Bu)_3$, $P(c-C_6H_{11})_3$, and PPh_3 derivatives of iron pentacarbonyl in high yield. Their approach in achieving high yields was based on the method developed by Strohmeier and Mueller; however, due to a large excess of ligand, 4 - 5 equivalents of phosphine, and their choice of solvent[14] the disubstituted product is formed exclusively. A cyclohexane solution containing the reactants is irradiated for 5 - 15 hours, with the irradiation time depending on the ligand. The product precipitates from the solution while unreacted starting material as well as monosubstituted derivatives of iron pentacarbonyl are soluble. After completion of the reaction the desired product is obtained in high purity requiring no further purification.

Therien and Trogler demonstrated with their work that the yields for the photochemical preparation of iron pentacarbonyl derivatives can be improved significantly if the

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reaction conditions are optimized according to the criteria outlined by Strohmeier in his review article[14] in 1964. Under optimized reaction conditions the photochemical preparation of iron pentacarbonyl derivatives from the readily available $Fe(CO)_5$ provides a method giving high yields and a high degree of selectivity in the case of the disubstituted product. An important feature in the photo-chemical preparation of disubstituted product is the purity of the obtained compound, which requires no further purifi-cation.

2.1.3 Combination of Photochemical and Thermal Reactions

In 1973 Conder and Darensbourg[15] introduced a method for the synthesis of group V substituted derivatives of iron pentacarbonyl. They were able to prepare an extensive series of $Fe(CO)_4L$ complexes in high yield by a combination of photochemical and thermal reactions using $Fe(CO)_5$ both as solvent and reactant. In their reactions the ligand was added to pure iron pentacarbonyl in an approximately 1 to 15 molar ratio. Irradiation of the reaction mixture for 2 hours at room temperature by a 450-watt Ace-Hanovia mercury arc lamp was followed by a reflux without irradiation period at 150 $^{\circ}C$ for one hour. After a final reflux plus irradiation period the excess iron pentacarbonyl was removed and the products were worked up and separated.

Reaction conditions for each ligand were selected to optimze the yield of the monosubstituted derivative of iron pentacarbonyl. The preparations performed by Conder and Darensbourg utilize the reaction scheme I. Although the scheme shows the monosubstituted derivatives to be the sole products, in most cases where phosphines were used as ligands the disubstituted product remained as a prominent impurity ranging from a zero to 31 % yield, based on the phosphine ligand. Except for the case of PPh_3, which was prepared selectively in a 85 % yield, separation of the obtained mixture of mono- and disubstituted products was required.

Scheme I

$$Fe(CO)_5 + L \xrightarrow{h\nu} Fe_2(CO)_9 + Fe(CO)_4L + Fe(CO)_3L_2$$

$$\downarrow L \quad heat$$

$$Fe(CO)_4L + Fe(CO)_3L_2$$

$$+ Fe(CO)_5 \downarrow heat, h\nu$$

$$Fe(CO)_4L$$
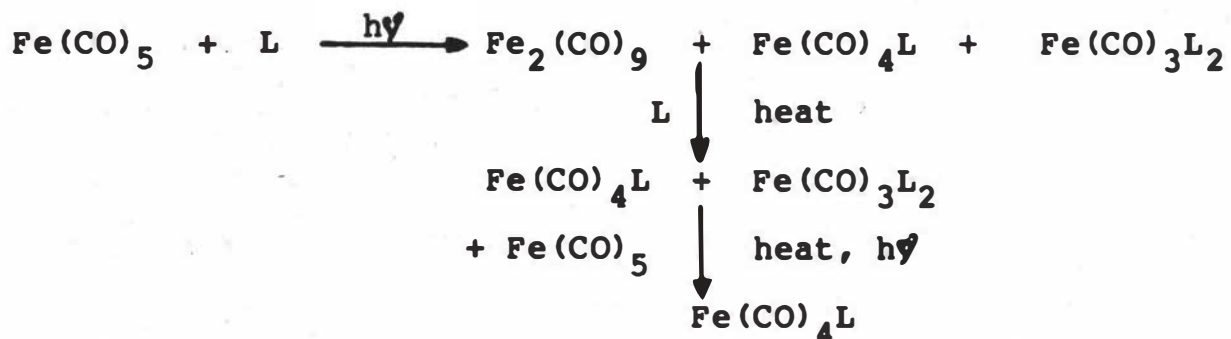
Thus, the method developed by Conder and Darensbourg provides a means to achieve high yields in the case of monosubstituted group V derivatives of iron pentacarbonyl; however, it still suffers from a lack of selectivity in the case of phosphine ligands despite the large excess of $Fe(CO)_5$.

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I.2.2 Catalyzed Substitution Reactions of Iron Penta-
    carbonyl

In the attempt to prepare substituted derivatives of
$Fe(CO)_5$ a number of methods have been developed which
involve catalysts. The use of a catalyst is thought to
increase the selectivity of the reactions as well as the
yields. Furthermore, catalyzed reactions usually can be
performed under milder reaction conditions and have shorter
reaction times.

2.2.1 Catalysis by Polynuclear Iron Carbonyl Anions

In 1979 Susan Beda Butts and D. F. Shriver[16] reported
that polynuclear iron carbonyl anions activate iron penta-
carbonyl towards substitution. They developed their
findings into a specific method for the preparation of
PPh_3, $P(OMe)_3$, and $P(OPh)_3$ monosubstituted derivatives of
iron pentacarbonyl. Their method involved the in situ pre-
paration of a catalytic amount of $Fe_2(CO)_8^{2-}$ by the ad-
dition of a 0.1 M solution of sodium benzophenone ketyl in
dry THF to a mixture of iron pentacarbonyl and the ligand.
At first a yellow precipitate of $Na_2Fe_2(CO)_8 \cdot xTHF$ formed,
which catalyzed the reaction of the remaining iron penta-
carbonyl and the phosphine or phosphite ligand during a
reflux period under nitrogen. In the case of PPh_3 the

monosubstituted product was obtained in a 69 % yield (based on the ligand) after destruction of the catalyst and re-crystallization.

A series of reactions in which catalytic amounts (0.45 to 0.5 equivalents) of PPN^+ salts of the dianions $Fe_2(CO)_8{}^{2-}$, $Fe_3(CO)_{11}{}^{2-}$, or $Fe_4(CO)_{14}{}^{2-}$ were added to a CH_3CN solution containing iron pentacarbonyl and PPh_3 gave yields of ca. 50 % under various thermal conditions, which were dependent on the dianion. Interestingly, the direct reaction of ligand with polynuclear dianions yielded disub-stituted product only, with decreasing yields as the cluster size increased. The obtained yields were 37 %, 32 %, and 22 % for the di-, tri-, and tetranuclear dianion (yields based on one $Fe(CO)_3(PR_3)_2$ per one iron atom). In addition two sets of control reactions were run. The first set of reactions was performed to show that iron penta-carbonyl does not react with ligand under various thermal conditions, while in the second set it was shown that no conversion of $Fe(CO)_3(PPh_3)_2$ to $Fe(CO)_4PPh_3$ occurred in the presence of iron pentacarbonyl.

From their experiments Butts and Shriver were not able to determine the exact mechanism of their substitution reaction. However, they excluded the possibility of a direct reaction of triphenyl phosphine with the dianions and subsequent Fe-Fe bond cleavage to yield the monosubsti-tuted product. Due to their reaction conditions they con-sidered the involvement of an unstable polynuclear inter-

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mediate or transition state likely. Even though the cata-
lytic property of the dianions was not proved, it seems
very likely, and the fact remains that the monosubstituted
PPh$_3$ derivative of iron pentacarbonyl is obtained uncon-
taminated by Fe(CO)$_3$(PPh$_3$)$_2$, in good yield, and after a
short reaction time. It can also be expected that the
method will work for a number of other ligands.

2.2.2 Transition Metal-Catalyzed Reactions

A new approach for the synthesis of mono- and disub-
stituted derivatives of iron pentacarbonyl was introduced
by Albers, Conville, Ashworth, and Singleton[17] at the
beginning of this decade. They reported a synthesis that
involves transition metal salts, most notably CoX$_2$. n H$_2$O
(X = Cl, Br, I), which readily catalyze the reaction bet-
ween iron pentacarbonyl and a series of phosphine ligands.
The main products after a reaction time of 0.5 to 6 hours
were of the type Fe(CO)$_4$PR$_3$ and were obtained in high
yield, hardly contaminated by Fe(CO)$_3$(PR$_3$)$_2$. In the cases
of PPh$_3$, PPh$_2$Me, and PPhMe$_2$ the disubstituted derivatives
were also prepared, using CoI$_2$. 4 H$_2$O as a catalyst.
However, the preparation of the disubstituted products
required a reaction time of twenty-four hours or more and
gave only moderate to poor yields.

All reactions involving the synthesis of Fe(CO)$_4$PR$_3$

were performed in refluxing toluene with an iron pentacarbonyl/ligand ratio of 2/1. The amount of catalyst accounted for 0.03 equivalent with respect to the ligand. Unreacted ligand and the cobalt salt were removed by column chromatography prior to removal of excess iron pentacarbonyl and solvent on a rotary evaporator. Recrystallization from CH_2Cl_2/hexane was only performed where necessary. Obtained yields ranged from 38 % for $Fe(CO)_4P(n-Bu)_3$ to 99 % for $Fe(CO)_4PPh_3$. The disubstituted derivatives of iron pentacarbonyl were prepared from either iron pentacarbonyl and two equivalents of phosphine ligand in the presence of 0.03 equivalent of $CoI_2 \cdot 4 H_2O$ or from $Fe(CO)_4PPh_3$ and one equivalent of triphenyl phosphine in the presence of 0.1 equivalent of $CoI_2 \cdot 2 H_2O$. In those cases where iron pentacarbonyl was used as starting material the reactions were run in methyl ethyl ketone, a solvent from which the disubstituted product precipitates during the reaction.

As in the catalyzed reaction described above the exact nature of the catalyst in solution is unknown. Due to changes in color during the course of the reaction the catalytic species are thought to be complexes of the general formula $CoX_2(PR_3)_2$ (X = Cl, I) formed from CoX_2 and phosphine in toluene.[18] This assumption is also supported by the addition of $CoCl_2(PPh_3)_2$ to iron pentacarbonyl and triphenylphosphine which gives similar color changes and catalysis. In analogy with earlier investigations made by the same authors on the substitution of CO by isonitriles

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on $M(CO)_6$ (M = Cr, Mo, W) with $CoCl_2 \cdot 2 H_2O$ as the catalyst,[19] a mechanism is suggested which involves attack of catalyst at coordinated CO to weaken the iron—CO bond. Subsequent loss of CO followed by an intermolecular process is thought to result in the monosubstituted product (scheme II). An intramolecular exchange of ligand between catalyst and metal carbonyl is considered unlikely. It was also found that the rate of the catalyzed reaction is strongly dependent on the anion in the transition metal salt as well as the phosphine ligand. This reactivity pattern is thought to be due to either steric or electronic effects or both in the cobalt catalyst or the catalyst-reagent interaction.[20]

Scheme II
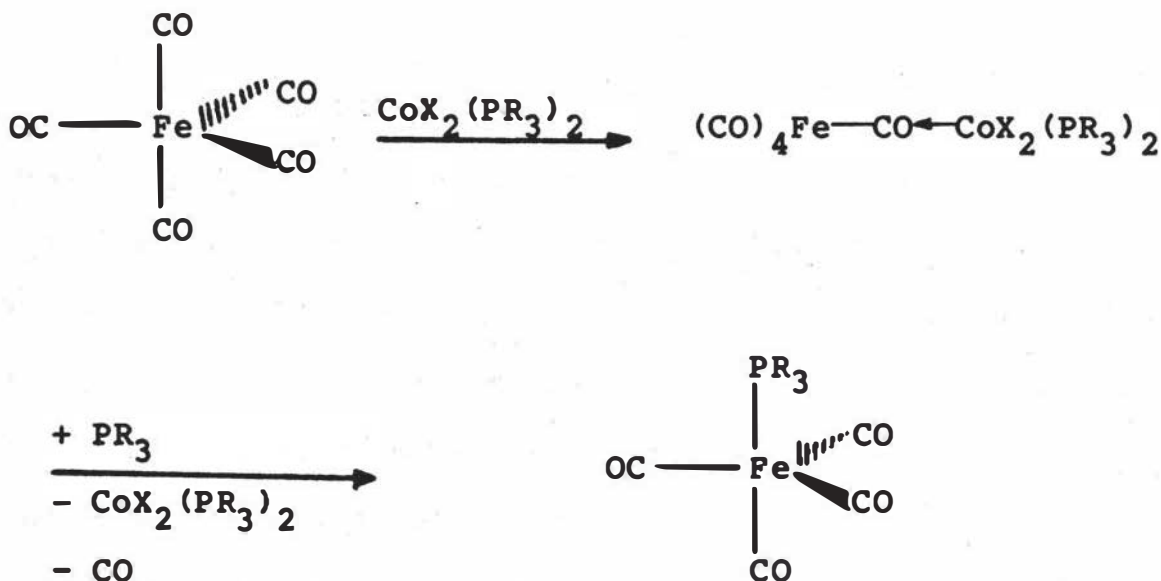
The transition metal-catalyzed reaction between iron pentacarbonyl and phosphine ligand just described provides

a facile, high-yield synthesis of monosubstituted phosphine derivatives of iron pentacarbonyl. The most important feature of this reaction is its high selectivity for the monosubstituted derivative, with less than 5 % of $Fe(CO)_3(PR_3)_2$ in the final reaction mixture. While the cobalt catalyst is most effective in the synthesis of monosubstituted product, only minimal catalysis of the transition metal salts was observed in the synthesis of $Fe(CO)_3(PR_3)_2$. These reactions were found to be slow and gave only moderate to poor yields in a variety of different solvents.

2.2.3 Hydride Facilitated Reactions

The last synthetic approach to be described in some detail involves the reaction of iron pentacarbonyl with hydride donors to yield the formyl complex $(HCO)Fe(CO)_4^-$, the hydride $HFe(CO)_4^-$, dianions $Fe(CO)_x^{2-}$ (X = 4, 3), or other iron complexes which might act as intermediates or catalysts or facilitate the substitution of iron pentacarbonyl in some other way.

The reaction between iron pentacarbonyl and sodium borohydride was first mentioned by Haworth and Huff[21] in the early sixties. Borohydride ion reacted with iron pentacarbonyl in diglyme under nitrogen at room temperature. An instantaneous reaction was evidenced by the formation of a

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deep red solution indicating the presence of polynuclear iron complexes, as well as the formation of a gas, which was identified to be H_2 and CO. Identification of any single iron carbonyl species in the crude reaction mixture by infrared analysis was found to be impossible by Haworth and Huff due to the complexity of the reaction mixture. The authors also reported that sodium borohydride can be replaced by $NaBH(OCH_3)_3$. However, in this case the reaction requires 4 to 8 hours to yield the deep red solution. In this place it should be noted that the reactions by Haworth and Huff were performed more than a decade before the formyl complex $(HCO)Fe(CO)_4^-$ was established, which seems important especially in the case where $NaBH(OCH_3)_3$ is used as the hydride source.

In 1975 Walter Siegl reported a hydride facilitated substitution of iron pentacarbonyl with neutral ligands.[22] With lithium aluminum hydride or sodium borohydride in refluxing THF as the hydride donor the method was developed into a high-yield synthesis for monosubstituted iron carbonyls. The synthesis of $Fe(CO)_4PPh_3$ was achieved by refluxing a reaction mixture containing $LiAlH_4$, PPh_3, and iron pentacarbonyl in molar ratios of 1 : 2 - 2.5 : 3 - 3.75 for 50 hours. Work-up of the crude reaction mixture by filtration through a short column of alumina, evaporation of the eluants and separation of the mono- and disubstituted products by column chromatography gave the monosubstituted derivative in a 60 % yield. No disubstituted product was

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isolated in this case. However, from the ratio of v(CO) for the E mode of $Fe(CO)_4PPh_3$ and the E' mode of $Fe(CO)_3(PPh_3)_2$ the ratio of $Fe(CO)_4L/Fe(CO)_3L_2$ in the crude reaction mixture was calculated to be 10. The compound $Fe(CO)_3(PPh_3)_2$ was prepared in two different ways using iron pentacarbonyl or $Fe(CO)_4PPh_3$ as starting material. (A). $LiAlH_4$ (30 mg), PPh_3 (5 mmol), and $Fe(CO)_5$ (1.5 mmol) were refluxed for 12 hours in 7 ml of THF after which all of the iron pentacarbonyl had reacted. An additional 10 mg of $LiAlH_4$ was added after 12 and 36 hours and the reaction was stopped after a total reaction time of 50 hours. After evaporation of the solvent in an open beaker and extraction of the residue with THF, the disubstituted derivative of iron pentacarbonyl was precipitated with H_2O to give a yield of 71 %. (B). Reaction of $Fe(CO)_4PPh_3$ and triphenylphosphine in a molar ratio of 1 : 2 in the presence of lithium aluminum hydride gave a yield of 44 % of $Fe(CO)_3(PPh_3)_2$ after a reaction time of 68 hours. Similar yields were obtained when $NaBH_4$ was used as substitution promotor.

The ability to control the degree of substitution of iron pentacarbonyl is the most important feature of Siegl's work. While the yield of monosubstituted product is high, only moderate yields were obtained for disubstituted products. One obvious disadvantage of Siegl's synthesis is the long reaction time, which is required to obtain good yields.

Even though no mechanism was suggested for the substi-

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tution reaction, a series of experiments was run to eluci-
date the course of the reaction. Initially, the reaction
was thought to proceed according to scheme III, equations
(7) to (10). In one experiment the hydride complex (equa-
tion 8) was treated with phosphine ligand under the same
conditions as described above; however, no reaction
occurred over a period of 2.5 days whether reducing agent
was present or not. Thus, the hydride was considered an
unlikely intermediate in the substitution reaction under
the given reaction conditions by Siegl. Although infrared
bands were observed in the appropriate regions (2000, 1935,
1910, 1565 cm^{-1}) which could be assigned to the formyl
complex (equation 7), attempts to isolate $HCOFe(CO)_4^-$ were
unsuccessful, which might, however, be due to the conver-
sion of formyl complex to the hydride complex under the
conditions of the work-up.

Scheme III

$$Fe(CO)_5 \; + \; H^- \; \rightleftharpoons \; HCOFe(CO)_4^- \tag{7}$$

$$HCOFe(CO)_4^- \; \longrightarrow \; HFe(CO)_4^- \; + \; CO \tag{8}$$

$$HCOFe(CO)_4^- \; + \; L \; \rightleftharpoons \; HCOFe(CO)_3L^- \; + \; CO \tag{9}$$

$$HCOFe(CO)_3L^- \; \longrightarrow \; H^- \; + \; Fe(CO)_4L \tag{10}$$
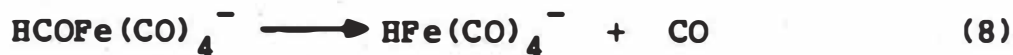
At higher concentrations of LiAlH$_4$ (1.25 mmol/1.5 mmol iron pentacarbonyl) it was found that a rapid reaction takes place between the reducing agent and iron pentacarbonyl. In the presence as well as the absence of ligand, 1/2 to 2/3 of the iron pentacarbonyl is converted to other carbonyl products, which were tentatively labeled as the formyl complex, the hydrido complex, and a polynuclear carbonyl complex, the latter causing the reaction mixture to have a red color (compare reference 21). It should be noted that this reaction was run under a CO atmosphere, while all other reactions were carried out under argon. Addition of ligand resulted in the formation of monosubstituted product from the remaining iron pentacarbonyl, but the other carbonyl products, derived from the action of LiAlH$_4$ on iron pentacarbonyl, remained unchanged. The information derived from these experiments led Siegl to the conclusion that the formyl complex is an unlikely intermediate in the substitution reaction. An experiment to elucidate the reactivity of the formyl complex towards substitution was not performed (equations 9 and 10).

From the experiments performed by Siegl it is now known that low concentrations of LiAlH$_4$ or NaBH$_4$ promote monosubstitution of iron pentacarbonyl in the presence of ligand, whereas iron pentacarbonyl fails to react with ligand by itself. Furthermore, it was shown that monosubstituted iron pentacarbonyl can be converted to the disubstituted derivative in the presence of ligand under

reducing conditions.

More insight into the reaction mechanism of hydride promoted reactions is provided by the work of Winter, Cornett, and Thompson[23] which was published in 1977. These authors report reactions of iron pentacarbonyl with various hydride agents, such as boron and aluminum hydrides, to yield the complex tetracarbonylformylferrate(0) in THF at 25 ^{o}C in varying yields according to equation (11). In agreement with Siegl's work it was found that $LiAlH_4$ as well as $NaBH_4$ led to little conversion of iron pentacarbonyl to the corresponding formyl complex. However, use of stoichiometric amounts of $HB(OCH_3)_3^-$ resulted in a quantitative conversion of iron pentacarbonyl to the tetracarbonylformylferrate(0). Interestingly, the monohydride agents $KBH(OCH_3)_3$ as well as $LiBH(C_2H_5)_3$ and $KBH(C_2H_5)_3$, the latter led to conversions of 69 % and 65 %, could even be used in a two- to threefold excess without decreasing the yield of the formyl complex. Attempts to isolate a substituted formyl complex by the reaction of a monohydride donor and $Fe(CO)_4PPh_3$ were unsuccessfull. Using $KBH(OCH_3)_3$ as the reducing agent the authors were not able to isolate a substituted formyl complex, which could be formed according to equation (12). The existence of such a complex was, however, observed by Casey and Neumann[24] by NMR. In their experiment $HCOFe(CO)_3PPh_3^-$ was formed by treatment of $Fe(CO)_4PPh_3$ with $KHB(O-i-Pr)_3$ in THF.

$$Fe(CO)_5 + HAY_3^- \longrightarrow HCOFe(CO)_4^- + AY_3 \qquad (11)$$

$$Fe(CO)_4PPh_3 + HAY_3^- \longrightarrow HCOFe(CO)_3PPh_3^- + AY_3 \qquad (12)$$
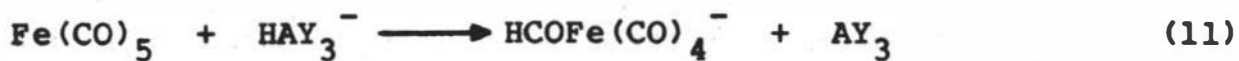
A = B or Al; Y = alkoxy or alkyl group

In addition to the methods described above mono- and disubstituted derivatives of iron pentacarbonyl have been synthesized from iron carbonyl halides under reducing conditions as well as from monoolefin iron tetracarbonyl complexes in the presence of donor molecules.[25]

I.3 Conclusion

It is apparent from the above overview of the synthetic methods of phosphine substituted derivatives of iron pentacarbonyl that a variety of different approaches is available to synthesize these compounds on a laboratory scale. However, most preparations suffer from at least one disadvantage such as lack of selectivity, low to moderate yields, long reaction times, or expensive promotors, catalysts, or starting materials. The most promising preparations to date are those involving transition metal-catalysts or hydride-promotors. Especially hydride facilitated reactions seem to be of particular interest due to their complex chemistry, which is not completely understood.

In the present work a hydride facilitated synthesis of trans-substituted phosphine derivatives is reported, giving high yields after extremely short reaction times. Further-

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more, attempts were made to elucidate the mechanism of the performed reaction.

Chapter II - Experimental

II.1 General Considerations

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was predried over calcium hydride and distilled from sodium and benzophenone. The commercially available butanol was found to be a mixture of isomers due to its range in boiling point (ca. 100 to 115.5 ^{O}C). Thus, the alcohol was distilled and only the fraction boiling beween 115 and 115.5 ^{O}C was used. All other solvents were used without further purification. However, all solvents were thoroughly purged with nitrogen before use. Iron pentacarbonyl, ligands, reducing agents, and other chemicals were obtained from various commercial suppliers and were used without further purification.

Melting and decomposition points were determined under vacuum in a sealed tube with a Thomas-Hoover Unimelt apparatus, and are reported uncorrected. A Nicolet 20 DX-B Fourier Transform Infrared instrument was used to record infrared spectra. The spectra were recorded under varying conditions depending on the sample under investigation. In general, the obtained spectra were expanded in the carbonyl region, ca. 2200 to 1700 cm^{-1}. ^{31}P NMR spectra were recorded using a 250 MHz Fourier Transform spectrometer of the University of Illinois, at Urbana-Champaign. In the spectra, which were recorded at 101 MHz, 85 % phosphoric

acid was used as an external standard (downfield is positive). The solvent varied depending upon the sample. ^{1}H NMR spectra were obtained on a Varian T-60 spectrometer from concentrated $CDCl_3$ solutions with tetramethylsilane as an internal standard. Mass spectra were recorded on a DuPont 21-490 mass spectrometer using samples with known fragmentation pattern to calibrate the m/e-axis.

2 Preparation of Substituted Iron Carbonyl Complexes

2.1 Preparation of $Fe(CO)_3(PR_3)_2$ Complexes

2.1.1 Method I

In the beginning the synthesis of trans-substituted phosphine derivatives of iron pentacarbonyl was accomplished by the following procedure. Approximately four equivalents of sodium borohydride (ca. 1.2 g) were added to 100 - 150 mL of 1-butanol, which had been purged with nitrogen. Then the solution was stirred for ca. 30 minutes at room temperature before one mL of iron pentacarbonyl (one equivalent) was added with a syringe. The addition of the iron carbonyl caused an immediate and intense evolution of gas. The next step in the course of the reaction was the addition of two equivalents of ligand to the crude reaction mixture before the solution was heated to reflux. The

ligands used were: tricyclohexyl-, tri(n-butyl)-, methyldiphenyl-, triphenyl-, diphenyl-, and diphenylvinylphosphine. Cooling of the crude reaction mixture after a reaction time of 18 +/- 2 hours resulted in a large amount of precipitate leaving only a thin layer of black supernatant. Filtration of the crude reaction mixture was found to result in considerable decomposition for most substituted complexes. Thus, the high boiling solvent was evaporated under reduced pressure with little heating. The obtained dirty white to brown residue was extracted after drying in a Soxhlet apparatus with dichloromethane under nitrogen. The extract was reduced in volume to about 20 mL and mixed with methanol. Different complexes required in general different chloroform/methanol mixtures to precipitate. The products were obtained pure after the described work-up as shown by melting points and by spectroscopic means. Yields and physical data for the individual complexes will be given in chapter III.

2.1.2 Method II

From the literature it was found that substitution reactions of iron pentacarbonyl require long reaction times (compare chapter I). A reaction time of approximately eithteen hours was thought to be reasonable at the beginning of the investigations. However, information derived from monitoring previous reactions suggested that much

shorter reaction times were sufficient. Thus, a number of reactions were performed with reaction times as short as twenty to thirty minutes giving good yields of disubstituted product. In these reactions all conditions, except for the reaction time, as well as the work-up remained unchanged. The obtained yields and physical data of the products will be given in chapter III.

2.2 Reactions Performed under Modified Conditions

In order to elucidate the course of the reaction, experiments were run that were expected to give information about the reaction mechanism as well as the conditions that are required for the formation of disubstituted iron pentacarbonyl derivatives in high yields.

2.2.1 Reaction of Fe(CO)$_5$ with PPh$_3$ in a 1:1 Ratio

Of particular interest was the interaction of iron pentacarbonyl with the reducing agent. In order to find out about the new species that form in the reaction mixture the following reaction was performed and monitored by infrared spectroscopy by taking samples from the crude reaction mixture in appropriate time intervals. Sodium borohydride (1.2 g, 4.17 equivalents) was added to 110 mL of 1-butanol. This solution was stirred under nitrogen for eighty

minutes at room temperature. When the iron pentacarbonyl (1 mL, 1.00 equivalent) was added with a syringe the reducing agent had not dissolved completely. Addition of the carbonyl complex resulted in an immediate and intense formation of gas. Furthermore, the color of the crude reaction mixture changed from a light yellow, which is the color of diluted iron pentacarbonyl, to dark yellow. After an additional two hours of stirring only a small amount of undissolved sodium borohydride remained and the solution appeared viscous. Upon heating the reaction mixture turned brown. After 30 minutes of refluxing one equivalent (1.99 g) of triphenylphosphine was added to the reaction mixture. The reaction was stopped thirty minutes after the addition of the ligand by removing the heating jacket. Since solutions of bis(triphenylphosphine) iron carbonyl derivatives are less air sensitive than solutions of other substituted iron pentacarbonyl derivatives, the work-up was modified compared to previous reactions. The crude reaction mixture in which a large amount of precipitate had formed after the addition of PPh_3 was cooled down to room temperature and stored in the freezer under nitrogen over night. The solution was filtered with suction and the obtained brownish precipitate was extracted with dichloromethane in a Soxhlet apparatus after drying leaving a white solid in the thimble. The obtained extract was reduced in volume to about 20 mL and mixed with an equal amount of methanol, which resulted in a yellow precipitate. After

storage under nitrogen in the freezer over night the solution was filtered with suction and the product was dried under vacuum.

The product was identified as $Fe(CO)_3(PPh_3)_2$ and its yield was found to be 68.3 % with respect to the ligand. In the carbonyl region of the infrared spectrum a very strong, split peak (1881.5 cm^{-1}, 1886.3 cm^{-1}) as well as a very weak absorption at 1972.9 cm^{-1} was observed for the compound in chloroform solution. The decomposition of the complex occurs between 268 and 272 ^{o}C.

The white solid which remained in the thimble after extraction with dichloromethane was the subject of further investigation. The results will be given and discussed in chapter III.

2.2.2 Preparation of $[(P(C_6H_5)_3)_2N^+][(CO)_4Fe(CHO)^-]$

In the attempt to prove the formation of the tetracarbonylformylferrate(0) anion from the reaction of iron pentacarbonyl with borohydride the complex was prepared as its bis(triphenylphosphine)iminium salt in situ. Bis(triphenylphosphine)iminium borohydride (4.44g, 8.02 mmol) was dissolved in 50 mL of 1-butanol under nitrogen at room temperature. When the iron pentacarbonyl (0.25 mL, 1.90 mmol) was added a vigorous evolution of gas occurred and a precipitate, which seemed to be of a white color in the almost colorless solution, formed immediately. The solvent

was stripped from the crude reaction mixture under reduced pressure and the residue obtained was dried. Several attempts to obtain crystals of the tetracarbonylformylferrate(0) salt by recrystallization from Et_2O/CH_2Cl_2 as described in the literature[26] failed. However, it was possible to observe the formyl complex by means of infrared spectroscopy.

2.2.3 $(CO)_4Fe(CHO)^-$-Decomposition (^{1}H NMR Experiment)

In the attempt to prove the participation of the anion $(CO)_4FeH^-$ in the reaction mechanism the following experiment was performed. Sodium borohydride (1.20 g = 31.6 mmol) was added to 30 mL of 1-butanol. After 15 minutes of stirring $Fe(CO)_5$ (1.00 mL = 7.61 mmol) was added to the solution with a syringe, which caused a vigorous reaction. The first ^{1}H NMR spectrum was taken after the reaction mixture had been stirred under nitrogen for approximately thirty minutes. The formyl hydrogen of the complex $(CO)_4Fe(CHO)^-$ was observed at a chemical shift of 14.65 +/- 0.1 ppm. The crude reaction mixture was heated with constant stirring and under nitrogen to a temperature of 70 $^\circ$C for half an hour on the next day. After cooling under nitrogen a second ^{1}H NMR spectrum of the crude reaction mixture was taken. The spectrum obtained did not only show the presence of the formyl complex but also the presence of the hydrido complex, $(CO)_4FeH^-$, which exhibits a chemical shift of negative 9.93 +/- 0.1 ppm for the hydride. Two days later the

crude reaction mixture was heated again for an additional
hour. The spectrum which was obtained showed the hydrido
species, but not the formyl complex.

2.2.4 Reaction of Tetracarbonylhydridoferrate(0)

To show that trans-substituted phosphine derivatives
of iron pentacarbonyl can be prepared from tetracarbonyl-
hydridoferrate(0) anion a reaction sequence was performed
that involved the preparation of tetracarbonylhydridofer-
rate(0) anion, $(CO)_4FeH^-$. A solution of $Na((CO)_4FeH)$ was
prepared according to a literature procedure[27], which is
described below. Sodium hydroxide (ca. 1.0 g, 25 mmol) was
dissolved in 3 mL of H_2O after which 3.5 mL of methanol
were added. Nitrogen was bubbled through this solution for
30 minutes before 0.7 mL of iron pentacarbonyl (5.2 mmol)
were added by syringe. The reaction mixture was stirred at
room temperature for 30 minutes after which unreacted MeOH,
H_2O, and $Fe(CO)_5$ were removed in vacuo.

The remaining $Na((CO)_4FeH)$, which was of a white to
light brown color, was worked up in two different ways in
different experiments. In one case the residue after evapo-
ration of methanol, water, and iron pentacarbonyl was ex-
tracted six times with 25 mL of 1-butanol. The extract
obtained was of a dark red color due to the presence of
anionic polynuclear iron hydride species which were also
observed in the IR spectrum. Triphenylphosphine

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(2.83 g, 10.8 mmol) was added to the extract which was
then heated to reflux under nitrogen. A few minutes after
the reaction mixture had started refluxing a yellow preci-
pitate had formed and the red color of the anionic polyiron
compounds had disappeared. After a reaction time of 40
minutes the crude reaction mixture was cooled down to room
temperature and stored in the freezer overnight. After
filtration the yellow product obtained was washed with
MeOH. The identity and purity of the product were confirmed
by its melting point and IR spectrum.

In the second case the $Na((CO)_4FeH)$ residue was ex-
tracted with 6 x 10 mL of THF. The combined extracts were
of a dark red color. Again, the IR spectrum showed the
presence of anionic polynuclear iron hydride species. After
evaporation of the THF 140 mL of 1-butanol were added to
the obtained dark red almost black residue and the solution
was heated to reflux after addition of triphenylphosphine
(2.810 g, 10.71 mmol) for thirty minutes. The disubstituted
triphenylphosphine derivative of iron pentacarbonyl was
obtained pure after filtration and washing with methanol. A
second batch of product was obtained from the reduced
filtrate. The identity and purity of the product were con-
firmed by its melting point and IR spectrum.

2.2.5 Preparation of $Fe(CO)_3(PPh_3)_2$ in Ethanol

The preparation of $Fe(CO)_3(PPh_3)_2$ was carried out
successfully in the alcoholic solvent 1-butanol. Thus, an

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analogous reaction was performed in the lower boiling solvent ethanol. The sodium borohydride (1.20 g, 31.6 mmol) was dissolved in ethanol and iron pentacarbonyl (1.00 mL, 7.61 mmol) was added with a syringe under nitrogen, which caused a vigorous evolution of gas as observed in previous reactions performed in 1-butanol. After the evolution of gas had stopped triphenylphosphine (4.00 g, 15.2 mmol) was added to the reaction mixture and the solution was heated to reflux under nitrogen for a period of five hours. Cooling of the reaction mixture under nitrogen in the freezer gave the yellow, crystalline product, which was washed with methanol after filtration of the crude reaction mixture. A second batch of product was obtained from the filtrate after mixing with methanol. The product was characterized by its infrared spectrum and melting point. The yield of the recrystallized product was found to be poor (14.0 %) compared to the reactions performed in 1-butanol.

2.2.6 Investigation of the Gaseous Side Products

In order to determine the composition of the gas which evolved upon addition of iron pentacarbonyl to a solution of sodium borohydride in 1-butanol, several reactions were

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run in which the gas was collected. In these experiments the gas was collected by allowing it to pass into a flask which had been rinsed with nitrogen. When the evolution of gas slowed down the flask was sealed and the collected gas was used for analysis.

Mass spectra recorded on a DuPont 21-490 mass spectrometer using samples of known fragmentation patterns for calibration did not contribute to the elucidation of the composition of the gas. Infrared spectra of the gas were obtained by expanding a sample of the gas into an evacuated gas cell. The obtained spectra indicated the presence of 1-butanol, iron pentacarbonyl, and traces of carbon monoxide. It was rather unlikely that all of the gas consisted of these three compounds. Thus, a sample of the gas was expanded into an evacuated container. Cooling part of the container with liquid nitrogen resulted in only a small decrease in pressure in the closed system indicating that most of the gas is hydrogen. The volume of the formed hydrogen was determined by collecting the gas in an inverted graduated cylinder under deionized water (1.78 l STP).

The obtained spectra and data will be given and interpreted in chapter III.

3 Attempted Preparations

3.1 Photochemical Preparation of $Fe(CO)_3(PPh_2CHCH_2)_2$

Initially the synthesis of bis(diphenylvinyl)iron(0)-tricarbonyl was attempted according to equations (5) and (6) (compare I.2.1.2, p 6) in THF with an excess of ligand. A schematic drawing of the reaction vessel is given in appendix B. After the reaction vessel had been rinsed with nitrogen it was filled with 2.0 mL (15.3 mmol, 1.0 equivalent) of iron pentacarbonyl, 9.75 mL (46 mmol, 3.1 equivalents) of diphenylvinylphosphine, and 200 mL of THF, which had been purged with nitrogen. The chemicals were added to the reaction vessel in the given order. This reaction mixture was irradiated for a period of two hours with a 500-Watt mercury arc lamp. An attempted work-up of a 50 mL-probe of the crude reaction mixture by evaporation of the solvent and subsequent recrystallisation from a mixture of benzene and petroleum ether showed that disubstituted and monosubstituted iron pentacarbonyl derivatives as well as polynuclear iron carbonyl species were present in the crude reaction mixture. An infrared spectrum of the crude reaction mixture taken in chloroform revealed that most of the iron pentacarbonyl had not reacted, which was concluded because of two strong absorptions in the carbonyl region of the infrared spectrum at 2021 and 1998 wavenumbers (compare diagram in appendix B at t = 2 hrs.).

In order to complete the reaction the crude reaction mixture was exposed to ultraviolet rays for another ten hours and the course of the reaction was monitored by infrared spectroscopy. Samples were taken every two hours, diluted with chloroform, and a spectrum was recorded. The spectra obtained at t = 6, 10, and 12 hours are shown in appendix B. A strong absorption band at 1883 wavenumbers indicates the presence of the disubstituted product. The monosubstituted derivative of iron pentacarbonyl could be identified by its absorptions at 2050, 1977, and 1945 wavenumbers. However, its concentration seems to remain low during the course of the reaction, which was concluded from the intensity of the absorption band at 2050 cm^{-1}. Important to note is the complex absorption pattern between 2000 and 1900 wavenumbers (terminal carbonyls) and below 1800 wavenumbers (bridging carbonyls) which strongly suggests the presence of polynuclear iron carbonyl species. After a total reaction time of twelve hours the solvent was evaporated to yield an oily black residue which formed a yellow, turbid solution if refluxed with hexane, leaving a porous black residue. The black residue was rejected. All attempts to isolate pure disubstituted product from the hexane solution failed. Even though a number of different solvents were used for recrystallization, most of the time a light brown powder was obtained indicating the presence of decomposition products; the pure product is of a clean yellow color.

In analysing the reaction conditions the following points were found to influence the result of the reaction in a negative manner. Under the conditions described the reaction time seems to be important. As can be seen from the spectra obtained, the amount of side products, namely polynuclear iron carbonyl species, which are detectable by their absorptions below 1800 wavenumbers due to their bridging carbonyl groups, increases with increasing reaction time. Furthermore, a prolonged period of irradiation of the crude reaction mixture results in an increase of decomposition products. The presence of these unwanted compounds can be concluded from the change in color from yellow to dark brown and the presence of a porous black residue after refluxing of the oily black residue, which was obtained after refluxing of the oily black residue obtained after evaporation of THF, in hexane. In addition, the solvent used was found to have a negative influence on the composition of the product mixture. The desired disubstituted product is soluble in THF. Thus, it remains in solution and is exposed to extensive irradiation. More favorable would have been a solvent in which $Fe(CO)_3(PPh_2CHCH_2)_2$ is insoluble. Insolubility of the product in the solvent used would result in precipitation of the desired product, shifting the reaction towards the formation of $Fe(CO)_3(PPh_2CHCH_2)_2$ and preventing unnecessary irradiation of already formed product, which would lower the amount of decomposition products present.

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3.2 Preparation of $Fe(CO)_3(AsPh_3)_2$

3.2.1 Preparation by Method I

In the attempt to prepare the compound $Fe(CO)_3(AsPh_3)_2$ iron pentacarbonyl was allowed to react with triphenylarsine under the same conditions as described under 2.1.1. However, after a period of reflux as short as twenty to thirty minutes the reaction mixtures turned completely black. Infrared analysis of the crude reaction mixture indicated the presence of only traces of _trans_-bis(triphenylarsine)tricarbonyliron(0). The disubstituted iron pentacarbonyl derivative was identified with reasonable certainty due to its carbonyl stretching band, which appears approximately 70 wavenumbers below a rather complex pattern of carbonyl stretching frequencies caused by other carbonyl species present in the solution.

3.2.2 Preparation under Modified Conditions

A second attempt was undertaken to prepare the trans-substituted triphenylarsine derivative of iron pentacarbonyl. As in the previous reactions the sodium borohydride (1.2 g, 32 mmol) was added to the 1-butanol (150 mL) and the solution was stirred for ca. 30 minutes under nitrogen. The addition of iron pentacarbonyl (1.00 mL, 7,61 mmol) caused a vigorous evolution of gas. After the formation of

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gas had stopped, triphenylarsine (4.65 g, 15.2 mmol) was added and the crude reaction mixture was stirred under nitrogen at room temperature for eighteen hours. During the following 98 hours the temperature of the crude reaction mixture was increased stepwise up to 105 $^{\circ}$C and the change in the composition of the solution was monitored by infrared spectroscopy. The spectra obtained and their contribution to the elucidation of the reaction mechanism will be discussed in chapter III. After a total of 116 hours the solvent was stripped from the crude reaction mixture under reduced pressure and the dark brown, almost black residue dried under nitrogen in a Soxhlet extractor producing a dark yellow solution. The dichloromethane was stripped from the extract on a rotary evaporator and the yellowish brown residue obtained dried under vacuum. Crystallisation from a CH_2Cl_2/hexane mixture[17] (1:2) yielded a small amount of yellow precipitate which was filtered with suction and washed with hexane. Infrared analysis of the product revealed that the precipitate consisted of triphenylarsine-tetracarbonyliron(0) as well as _trans_-bis(triphenylarsine)tricarbonyliron(0).

Chapter III - Results and Discussion

III.1 Yields and Physical Data

1.1 Summation of Experimental Results

The method proposed by Dr. R. L. Keiter to prepare trans-substituted phosphine derivatives of iron pentacarbonyl was investigated in a series of reactions. It was found that the applied method was capable of producing the desired product $Fe(CO)_3(PR_3)_2$ selectively for a variety of ligands. Even though the reaction conditions were not fully optimized, very good yields were obtained. For the ligands PPh_2CHCH_2 and PPh_3 reactions were run in which the reaction time had been optimized. Since an iron pentacarbonyl/ligand ratio of 1:2 was used giving excellent yields no attempts were made to increase the yields by using excess ligand. Furthermore, even with the ligand as the limiting reagent good yields were obtained which lead to the conclusion that the amount of ligand has little or no effect on the yields and selectivity. The reaction conditions were not optimized with respect to the amount of reducing agent. Most reactions were performed with a four-fold molar excess of sodium borohydride compared to the amount of iron pentacarbonyl. In order to estimate the effect of the solvent used on the yields a reaction was run in ethanol. A table containing the obtained yields and physical data of the synthesized complexes is given below.

Table III.1.1 Yields and Physical Data of $Fe(CO)_3(PR_3)_2$ Complexes (Part A)

Ligand	$\mathbf{v}(CO)^*$ $[cm^{-1}]$ (solv.)	$\mathbf{v}(CO)$ $[cm^{-1}]$ (solv.)	ref.	δ [ppm] (^{31}P)	δ [ppm] (^{31}F)	ref.
$P(C_6H_{11})_3$	1850 ($CHCl_3$)	1846 (CH_2Cl_2)	13	86.1	89.1	13
	1851 (CH_2Cl_2)					
$P(n-Bu)_3$	1860 ($CHCl_3$)	1873 br (hexane)	15	62.4	66.0	13
		1855 (CH_2Cl_2)	13			
		1872.3 (hexane)	28			
		1865.3 (THF)	28			
$PMePh_2$	1877 ($CHCl_3$)	1874 ($CHCl_3$)	17	64.7	–	–
PPh_2CHCH_2	1883 ($CHCl_3$)	1886 ($CHCl_3$)	29	76.4	75.9	29
		1884 (hexane)	29			
PPh_3	1884 ($CHCl_3$)	1885 (hexane)	8	82.5	78.2	13
		1887 ($CHCl_3$)	5			
		1883 ($CHCl_3$)	17			
		1878 (CH_2Cl_2)	13			
PPh_2H	1883 ($CHCl_3$)	–	–	53.9	–	–

*The given values represent an average of the split E mode.

Table III.1.1 Yields and Physical Data of $Fe(CO)_3(PR_3)_2$ Complexes (Part B)

dec. pt. $[°C]$ **	dec. pt. $[°C]$	ref.	rxn. time hrs.	yield $[\%]$ ***	Ligand
282 - 5	228	10	18	55.6	$P(C_6H_{11})_3$
	228	13			
53 - 5	53 - 5	15	18	47.3	$P(n\text{-}Bu)_3$
	55	13			
170 - 2	-	-	18	90.4	PPh_2Me
170 - 2	170 - 2	29	18	58.2	PPh_2CHCH_2
			3.5	64.9	
			0.75	66.0	
268 - 72	272	7	0.5	68.3[4*]	PPh_3
290 - 2[5*]	260	5		51.9[5*]	
	272	6	5.0	14.0[7*]	
	265 - 6	10	more than 10 days at RT + 1.5 hrs. at rf.	93.3[8*]	
168 - 70	-	-	19	92.3[6*]	PPh_2H

Attempts to prepare $AsPh_3$ trans-substituted derivatives of $Fe(CO)_5$ in reasonable yields failed.

** All melting points were determined under vacuum. *** Each yield represents an average. [4*] Only one equivalent of ligand was added to the refluxing reaction mixture. Yield was calculated with respect to the ligand. [5*] Prepared from hydrido species or "long time" reaction. [6*+8*] Not recrystallized, only washed with MeOH. [7*] Reaction performed in ethanol.

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1.2 Interpretation of Infrared Spectra

Phosphine trans-substituted derivatives of iron penta-carbonyl are most conveniently identified by infrared spectroscopy. Coordinated carbon monoxide exhibits intense stretching vibrations in a region (2100 cm^{-1} to 1500 cm^{-1}) which is fairly well isolated from other types of vibrations likely to be present. Furthermore, the carbonyl region can be subdivided into regions which allow prediction of the approximate structure of the complex under investigation. Terminal carbonyl ligands of neutral complexes can be observed between 2100 cm^{-1} and 1850 cm^{-1}, whereas bridging carbonyls (μ_2-CO) absorb in the 1860 to 1700 cm^{-1} region. Carbonyls coordinated to three metals (μ_3-CO) absorb below 1750 cm^{-1}. Besides structural information the location of the peak also provides information on the C-O bond order, with decreasing wavenumbers corresponding to decreasing bond orders. Thus, the frequencies of the carbonyl stretching vibrations also reflect the electron-donor properties of ligands in the complex. Ligands that donate a higher electron density to the metal than others cause an increased back donation into the π^* orbitals of the carbonyl ligands, and hence lower the bond order and stretching frequency.[30] This effect can be observed in comparing, e. g. the $P(C_6H_{11})_3$ and $P(n-Bu)_3$ substituted complexes with those substituted by PPh_3 or PPh_2CHCH_2, with the latter complexes exhibiting absorptions

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at higher wavenumbers due to the electron withdrawing properties of the substituents on the phosphorus, which cause a decrease in the electron density donated to the iron.

The derivatives of iron pentacarbonyl of the type $Fe(CO)_3(PR_3)_2$ are of D_{3h} symmetry. The two phosphine ligands occupy the two axial positions while the carbonyl ligands occupy the three equatorial positions. Formation of the trans diaxial complexes is attributed to more effective back π-bonding of the carbonyl ligands in the equatorial plane.[31, 32] Knowing the symmetry type of the iron carbonyl complexes enables the number of infrared active modes in the carbonyl region of the infrared spectrum to be derived by standard group-theoretical methods (compare appendix C), which lead to the following result. Only one stretching mode (E') is infrared active, while two bands, which are due to stretching modes, are observed in the Raman spectrum. Furthermore, two bending modes ($A_2"$, E') are infrared active. However, these vibrational modes appear below 700 wavenumbers in the IR spectrum and were not used in the identification of the synthesized compounds.

There is one other important feature observed in each of the spectra of phosphine disubstituted derivatives of iron pentacarbonyl taken in dichloromethane or chloroform which merits comment. In each of these spectra a splitting or at least a broadening of the E' stretching mode was observed, as well as a very weak and broad peak at

higher wavenumbers than the major product peak. These observations can be attributed to one effect, namely the lowering of the symmetry of the complexes. This deviation from the idealized point group of the molecule is caused by two factors, the bulkiness of the phosphine ligand and the interactions between the complex and the solvent in which the spectra were taken. Hence, the weak and broad peak is assigned to the infrared inactive A_1' mode which gains some allowdness due to the above reasons.[33] The splitting of the E' mode is attributed to the same effect that causes the observed A_1'-band.

In order to illustrate the above discussion the spectra of bis(tri-n-butylphosphine)tricarbonyliron(0) taken in dichloromethane (fig. 1) and chloroform (fig. 2), as well as a spectrum of bis(diphenylvinylphosphine)tricarbonyliron(0) (fig. 3) taken in chloroform are given below. The spectra shown were obtained from a thin film, between two sodium chloride windows, of a solution containing the complex under investigation. The given spectra are not only examples for peak broadening, peak splitting, and the gain of allowdness of the A_1' stretching mode, but also demonstrate the dependence of these observed effects on the solvent used. In the case of $Fe(CO)_3(PBu_3)_2$ the broadening of the E' mode is amplified to a splitting and the forbidden mode A_1' clearly gains intensity in changing the solvent from dichloromethane to chloroform.

44

Fe(CO)$_3$(PBU$_3$)$_2$ IN DICHLOROMETHANE

(fig. 1)

Minima List:
X- 1883.5 Y- 15.082
1 Minima Detected

WAVENUMBERS (CM-1)

%TRANSMITTANCE

45

Fe(CO)$_3$(PBu$_3$)$_2$ IN CHLOROFORM   (fig. 2)

Minima List:
X= 1054.1   Y= 7.7430
X= 1866.7   Y= 0.7670
X= 1954.7   Y= AU.078
3 Minima Detected

46
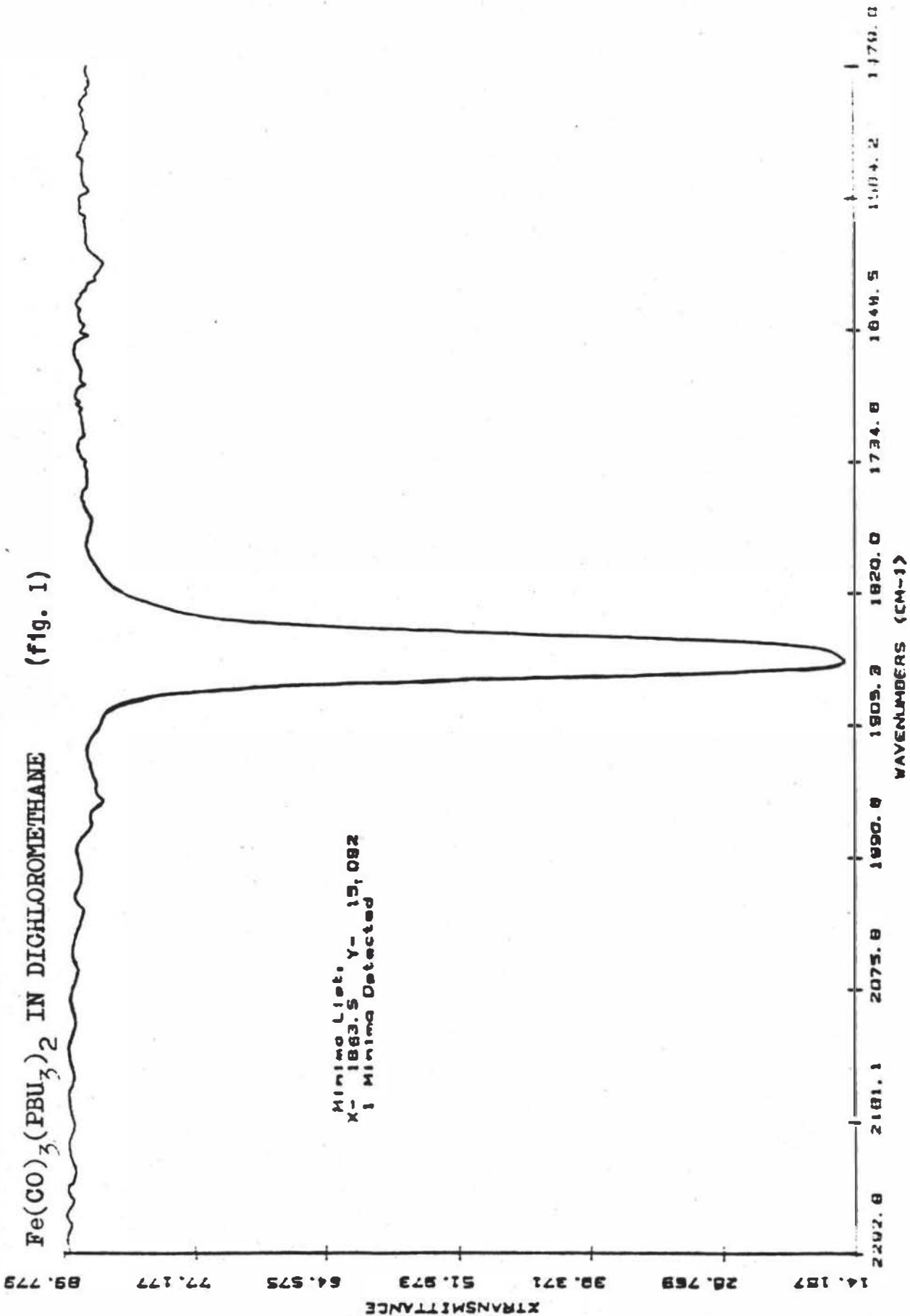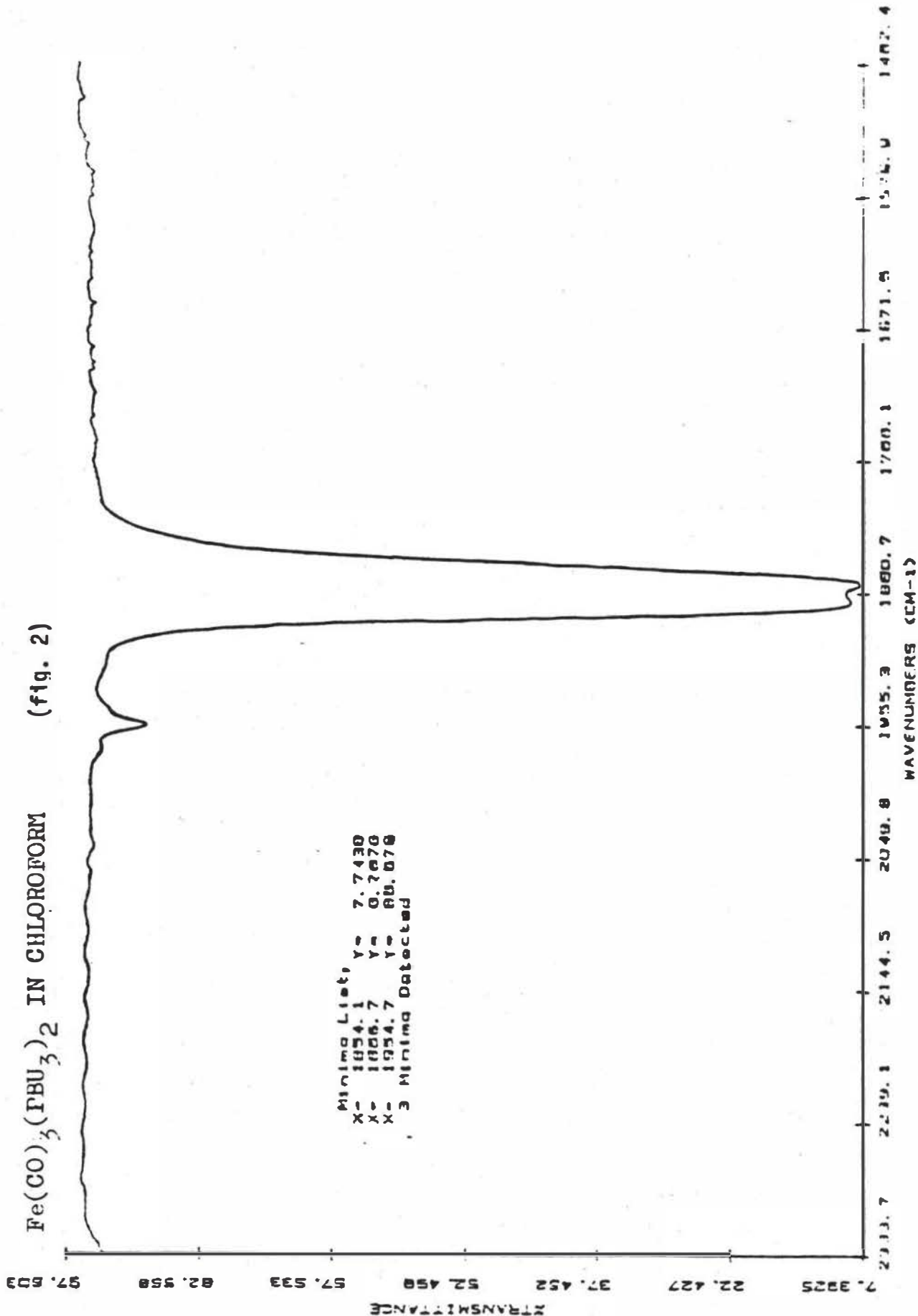
Fe(CO)₃(PPh₂CHCH₂)₂ IN CHLOROFORM

(fig. 3)

47
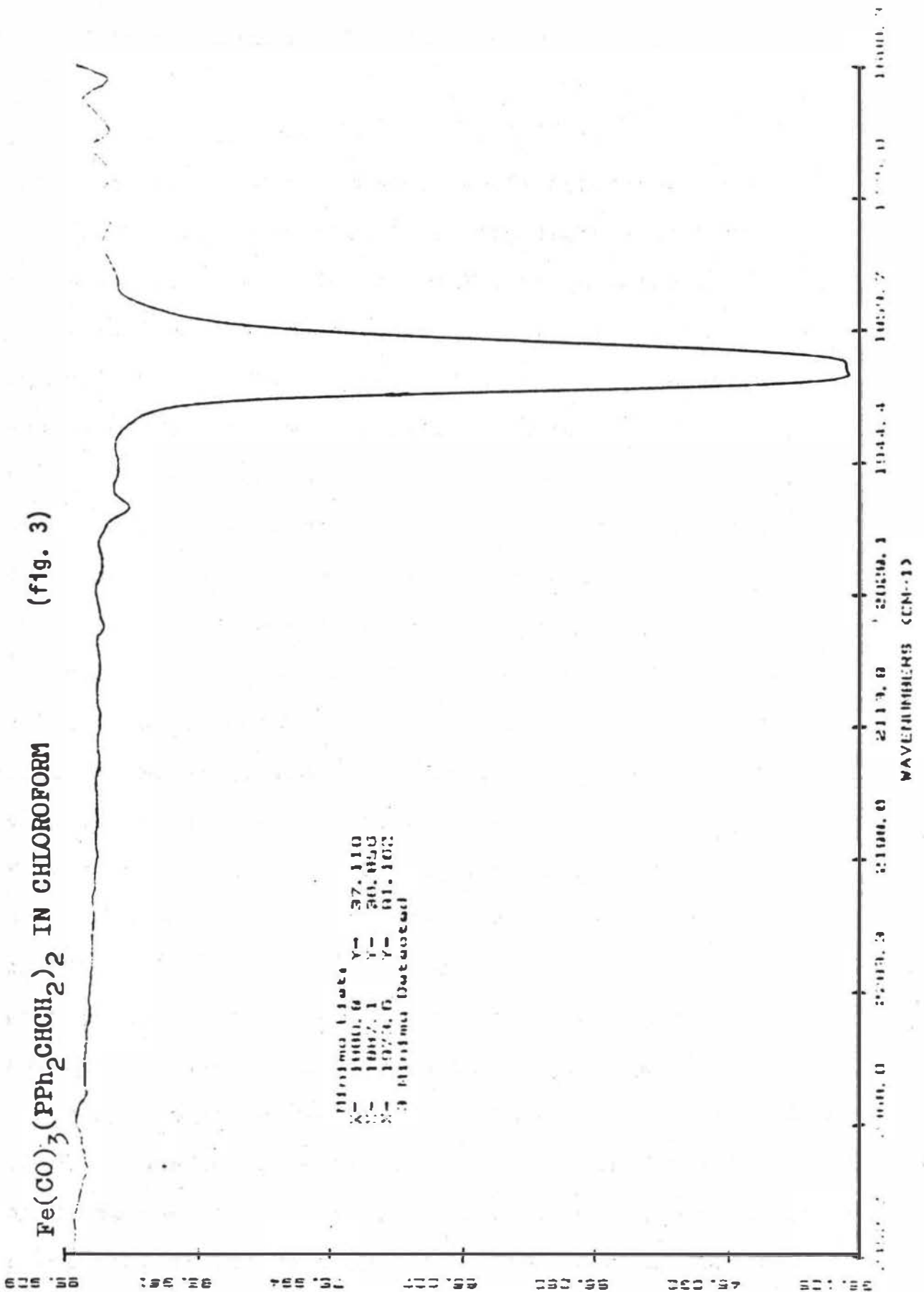
1.3 Interpretation of ^{31}P NMR Spectra

Besides infrared spectroscopy ^{31}P nuclear magnetic resonance was used to identify the synthesized products. ^{31}P is the only naturally occurring isotope of phosphorus and has a non-zero spin of I = 1/2 and a magnetic moment of μ = 1.1305 nuclear magnetons. Due to the I value of 1/2 the splitting patterns observed in a ^{31}P NMR spectrum are analogous to those we are familiar with from ^{1}H NMR spectra. However, chemical shifts are observed over a much wider range, approximately 500 ppm. This provides an excellent means of determining molecular structures of phosphorus-containing compounds. The sensitivity of the ^{31}P nucleus is much lower than the sensitivity of the ^{1}H nucleus, only 6.64 per cent that of the ^{1}H nucleus at constant magnetic field. However, this lack of sensitivity can be overcome by fourier transform spectroscopy. Fine structure on the ^{31}P resonance absorption bands arising from spin-spin interaction with other nuclei such as ^{13}C or ^{1}H are also observed. However, caused by the natural abundance of the ^{13}C the spin-spin interaction between ^{31}P and ^{13}C is neglectable.[34] In the complexes under investigation splitting of the ^{31}P signals can occur, which is due to spin-spin coupling between ^{31}P and ^{1}H. As an example to illustrate this phenomenon the diphenylphosphine complex has been chosen. The spectrum obtained (fig. 4), which was recorded under conditions as described

Fe(CO)$_3$(PPh$_2$H)$_2$ (COUPLED)   (fig. 4)

55.743 ppm

52.120 ppm

366.88 Hz

56   54   52   50   PPM

49
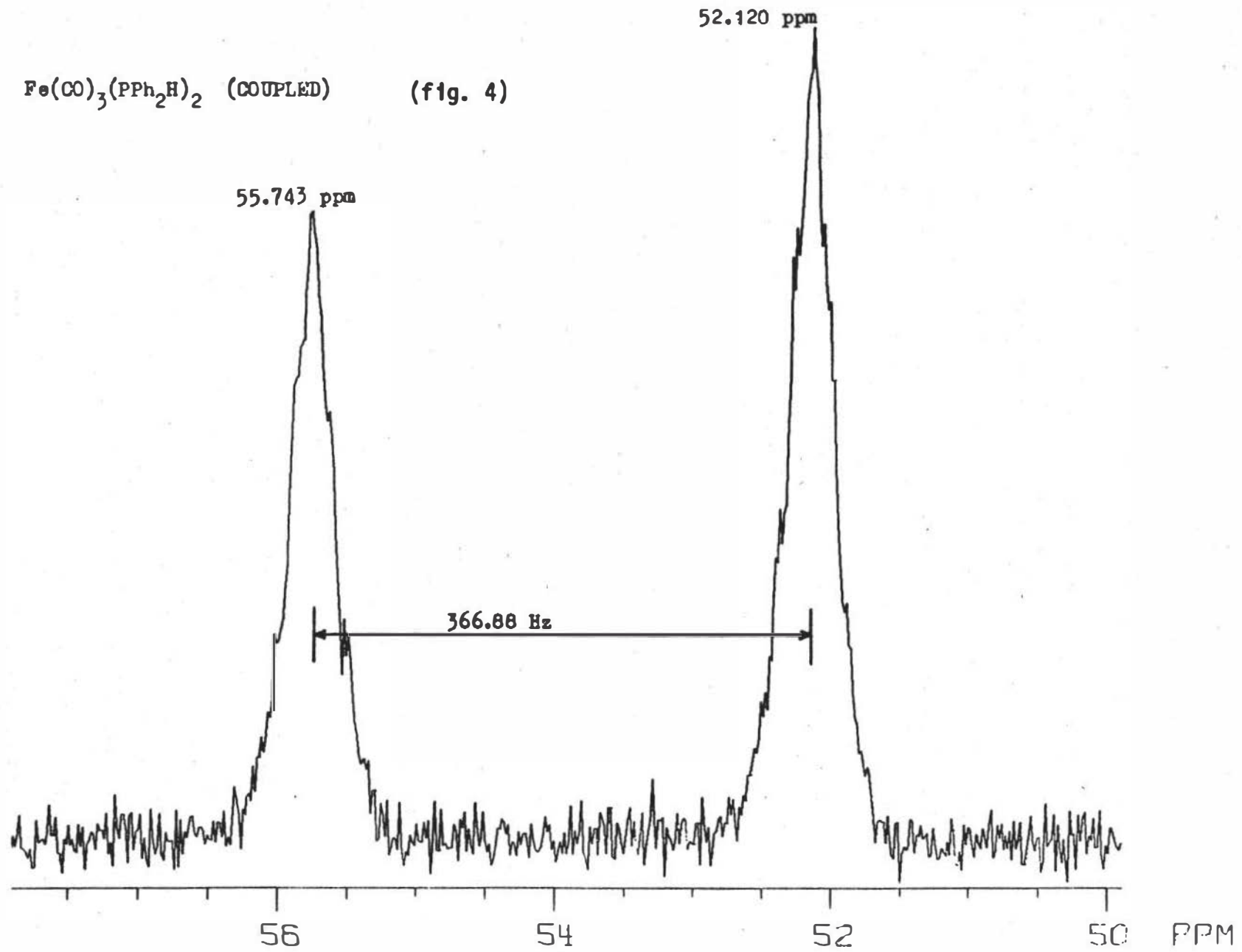
in the experimental section, is shown below. Two peaks of equal intensities are observed at 55.7 ppm and 52.1 ppm. The separation of these two peaks of 366 Hz (3.62 ppm) directly gives the coupling constant between the ^{31}P nucleus and the ^{1}H nucleus. The spectrum can be simplified by applying a technique which is known as the double resonance technique. This method is based on a continuous irradiation of the sample with a broad band at the resonance frequency of the ^{1}H nuclei. This permanent irradiation of the sample causes rapid alpha to beta and beta to alpha transitions in the ^{1}H nuclei which in turn eliminates the splitting observed in the ^{31}P NMR spectrum. A spectrum recorded from the complex $Fe(CO)_3(PPh_2H)_2$ using the double resonance technique is shown below (fig. 5). Only a single peak at 53.9 ppm is observed. As can be seen from the previous spectrum $Fe(CO)_3(PR_3)_2$ complexes give rise to rather simple ^{31}P spectra under the outlined conditions, which is due to the equivalence of the ^{31}P nuclei in the given complexes. For further illustration the spectrum of the bis(tricyclohexylphosphine)tricarbonyl-iron(0) complex is given below (fig. 6). This complex exhibits a chemical shift of the ^{31}P nucleus of 86.2 ppm. These two complexes represent the lower and upper values of chemical shifts observed in the recorded ^{31}P NMR spectra of the complexes under investigation. While chemical shifts in ^{1}H NMR spectra can be related to the electron density about the hydrogens as a function of inductive effects of

50

$Fe(CO)_3(PPh_2H)_2$ (DECOUPLED)   53.932 ppm

(fig. 5)
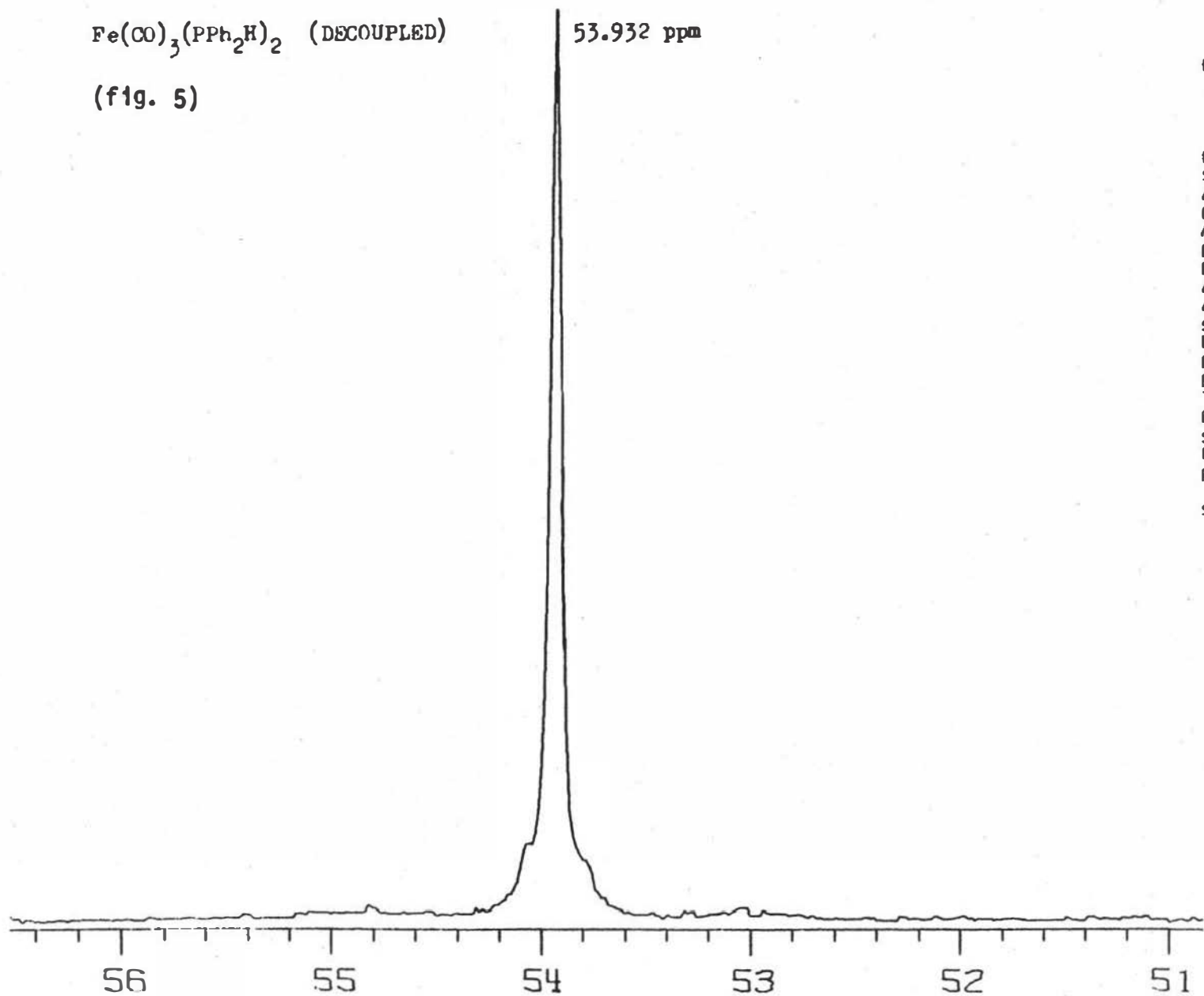
ONE-PULSE SEQUENCE

PZ=   40.00 USEC
DS=   1.00 SEC

NA =   200
SIZE = 65536
AI =   655.96 MSEC
OPO ON =   0
ABC ON
BUTTERWORTH FILTER ON
DB ATT.=   3
ADC =   12 BITS
AI =   11
SW = +/- 25000.0
DW =   20
RG =   40 USEC
DE=   50 USEC
TL HIGH POWER OFF
OF=   -747.64
SF=   101.265000
PA=   146.7
PB=   1011.1

SCALE   28.83 HZ/CM
      =   .2847 PPM/CM

51

56   55   54   53   52   51 PPM

Fe(CO)$_3$(P(c-C$_6$H$_{11}$)$_3$)$_2$ (fig. 6)

86.199 ppm

neighboring groupings no such correlations can be made between the chemical shifts of ^{31}P nuclei and the electronegativity of substituents. A more successful prediction of chemical shifts seems to be possible if such factors as bond angles, hybridizations, and bond orders are considered.[34] In the complexes under investigation in this study the chemical shifts covered a range of approximately 32 ppm, as can be seen in the table given above. ^{31}P NMR did not only provide a tool in identifying the various complexes, but also would have provided a limited means to detect unreacted ligand or other phosphorus containing contaminations in the products.

1.4 Miscellaneous

Besides the carbonyl absorption bands in the infrared spectrum and the chemical shifts of the phosphorus nuclei in the coordinated ligands the melting points were used as a third physical property to characterize the synthesized complexes.   All melting points were determined under vacuum in a sealed tube.   An observation which was made for all synthesized phosphine derivatives was that they decomposed upon melting or right after they had melted. The decomposition was apparent by an evolution of gas, most likely carbon monoxide, as well as a change in color from yellow to dark brown or black.   The melting point of a substance does not only contribute to the characterization of the substance under investigation, but also provides qualitative information on its purity.   Impurities usually result in a decreased melting point as well as an increase in the melting point range.   For most of the determined decomposition points good agreement was achieved with values reported in the literature.   However, in the case of the tricyclohexylphosphine derivative a melting point of 282 to 285 ^{O}C was determined. The same melting point was measured for product obtained from different reactions, which is considerably higher than the reported melting point of 228 ^{O}C.   Another point which has to be mentioned is that the triphenylphosphine derivative which was synthesized by method I or II had a melting point which was in good agree-

ment with the one reported in the literature. The same complex synthesized by the methods described under 2.2.4 in the experimental section of this paper exhibited a decomposition point which was 20 $^{\circ}$C higher than the decomposition points reported in the literature. No unequivocal explanation can be given for this observation.

All complexes have been found to be sensitive to air in solution. The rate of decomposition of the dissolved products was also found to depend on the ligand, with the triphenylphosphine derivative being the most stable complex. Solutions of this complex were worked up in the air without showing obvious signs of decomposition. Solutions of the other products darkened in their color if exposed to the air for more than a few minutes, indicating decomposition of the complex. However, if the products were dry and stored under vacuum no apparent decomposition took place.

All complexes were obtained pure after crystallization of the crude reaction products from a mixture of dichloromethane/methanol. Even though traces of phosphine monosubstituted derivatives of iron pentacarbonyl were observed in the crude reaction mixture, uncontaminated product was isolated. The obtained yields compare favorably with yields reported in the literature. A noteworthy feature of the presented synthesis is the extremely short reaction time.

III.2 Reaction Mechanism

2.1 Formation of Tetracarbonylformylferrate(0)

The first synthesis of a formyl complex was described
in 1973 by Collman and Winter.[35] These chemists reported
the preparation of the anionic formyl $(CO)_4Fe(CHO)^-$ from
the reaction of $Na_2Fe(CO)_4$ with formic acetic anhydride.
However, formic acetic anhydride unfortunately was found to
be not a general reagent for formyl complex synthesis.[23] As
shown by the work of Casey, Gladysz, and Winter in 1976 a
completely different approach for the synthesis of anionic
formyl complexes is available.[36] In general, anionic formyl
complexes can be prepared by the use of appropriate hydride
nucleophiles which are capable of nucleophilic attack of
coordinated carbon monoxide. For this purpose a number of
different boron compounds such as trialkylborohydrides and
trialkoxyborohydrides have been used. Results on the re-
duction of various neutral carbonyl complexes with a number
of different hydride donors published by Winter, Cornett,
and Thompson in 1977[22] showed that trialkylborohydrides and
trialkoxyborohydrides were most effective in the synthesis
of anionic formyl complexes from the corresponding neutral
carbonyl complexes. In the same study it was also shown
that reducing agents such as $LiAlH_4$, $NaBH_4$, and KH were
essentially useless in preparing the desired products.
The above information was derived by Winter, Cornett, and

Thompson from experiments performed at 25 $^{\circ}$C in THF. The nucleophilic substitution reaction of coordinated carbon monoxide with appropriate hydride sources can be written as shown in equation (13).

$$L_nM-CO \quad + \quad -\overset{|}{\underset{|}{B}}-H \quad \longrightarrow \quad L_nM^- \quad + \quad -B\diagup^{\diagup}_{\diagdown} \qquad (13)$$

$$\underset{H}{\overset{|}{C}}\diagup\diagdown O$$
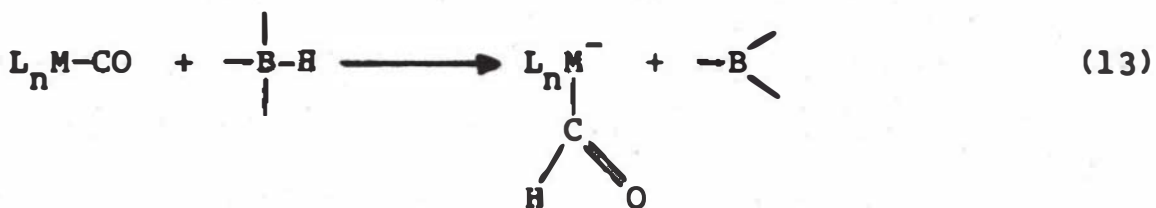
L = CO, n = 4 or 5, M = transition metal

Even though the formation of the tetracarbonylformyl-ferrate(0) anion seemed to be unlikely at first glance, due to the use of sodium borohydride as the reducing agent, this species was observed by infrared spectroscopy in the crude reaction mixture of the performed reactions. This observation can be accounted for by the choice of solvent. 1-butanol is capable of undergoing a reaction with the reducing agent under appropriate conditions (compare III.3 Investigation of the Gaseous Side Products). Thus, a mechanism might be considered in which the alcoholic solvent plays an important role in the initial step of the reaction under investigation. First spectroscopic evidence of the formation of the iron formyl complex shall be provided, followed by further experiments to establish the initial formation of the tetracarbonylformylferrate(0) anion. Finally, a solvent assisted mechanism will be proposed to account for the formation of the formyl species.

As mentioned earlier, the tetracarbonylformylfer-

rate(0) anion was observed by infrared spectroscopy in the crude reaction mixture. Below, two infrared spectra are shown labeled as "CARBONYL REGION OF FORMYLTETRACARBONYL-FERRATE(0) ANION" (fig. 7) and "CARBONYL REGION OF FORMYL COMPLEX" (fig. 8). The spectra were obtained under the following conditions. The first spectrum was obtained by mixing a sample of the crude reaction mixture, which was taken approximately one hour after iron pentacarbonyl had been added and before the reaction mixture was heated to reflux, with a tenfold excess of dichloromethane. The solution was filled into a sodium chloride cell and a spectrum of the film was recorded. The second spectrum was obtained from the same crude reaction mixture under identical conditions approximately 2 and 2/3 hours after the addition of iron pentacarbonyl, with the crude reaction mixture still at room temperature. By comparison with the literature the observed absorption bands in the carbonyl region at 2025.3 (m), 1935.5 (sh), and 1908.6 (s) cm^{-1} were assigned to the carbonyl vibrations of the tetracarbonyl-formylferrate(0) anion. Collman and Winter[35] reported absorptions in the IR spectrum at 2018 (w), 1930 (s), and 1902 (vs) cm^{-1} for the above complex recorded in THF. Considering the difference in the solvent used, or in the present case the mixture of solvents, the slight variation in the absorption frequencies can be explained by the difference in the interaction between the anionic formyl complex and the bulk solution. A shift to higher wavenum-

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CARBONYL REGION OF FORMYLTETRACARBONYLFERRATE(D) ANION   (fig. 7)

Minima List:
X= 1908.8   Y= 45.298
X= 2025.3   Y= 82.938
2 Minima Detected

SHOULDER AT 1935.5 CM-1

%TRANSMITTANCE

WAVENUMBERS (CM-1)

59

CARBONYL REGION OF FORMYL COMPLEX

(fig. 8)

Minima List:
X= 1810.0   Y= 85.923
X= 1936.0   Y= 78.433
X= 1984.7   Y= 85.188
X= 2025.2   Y= 82.184
4 Minima Detected

60
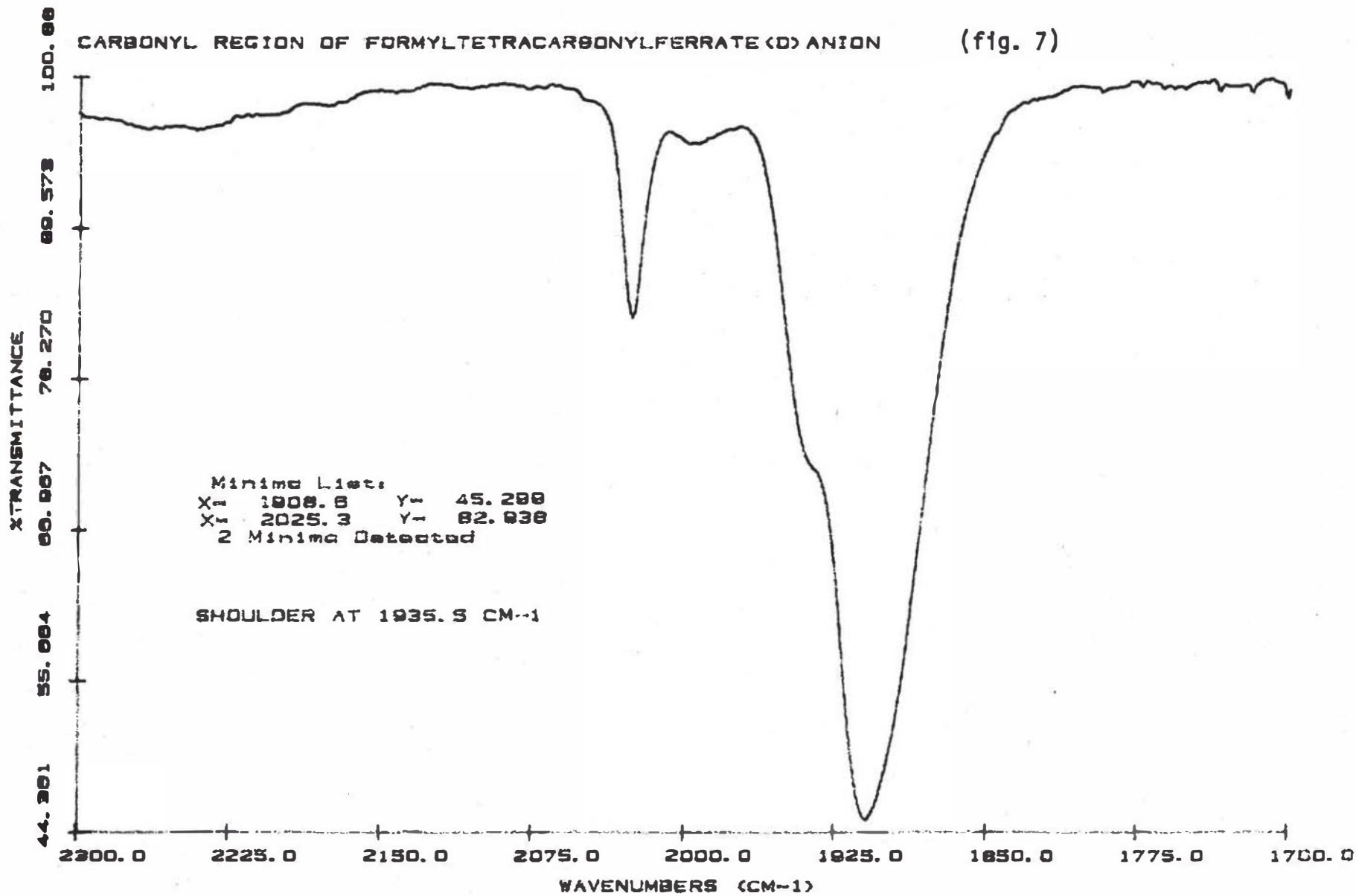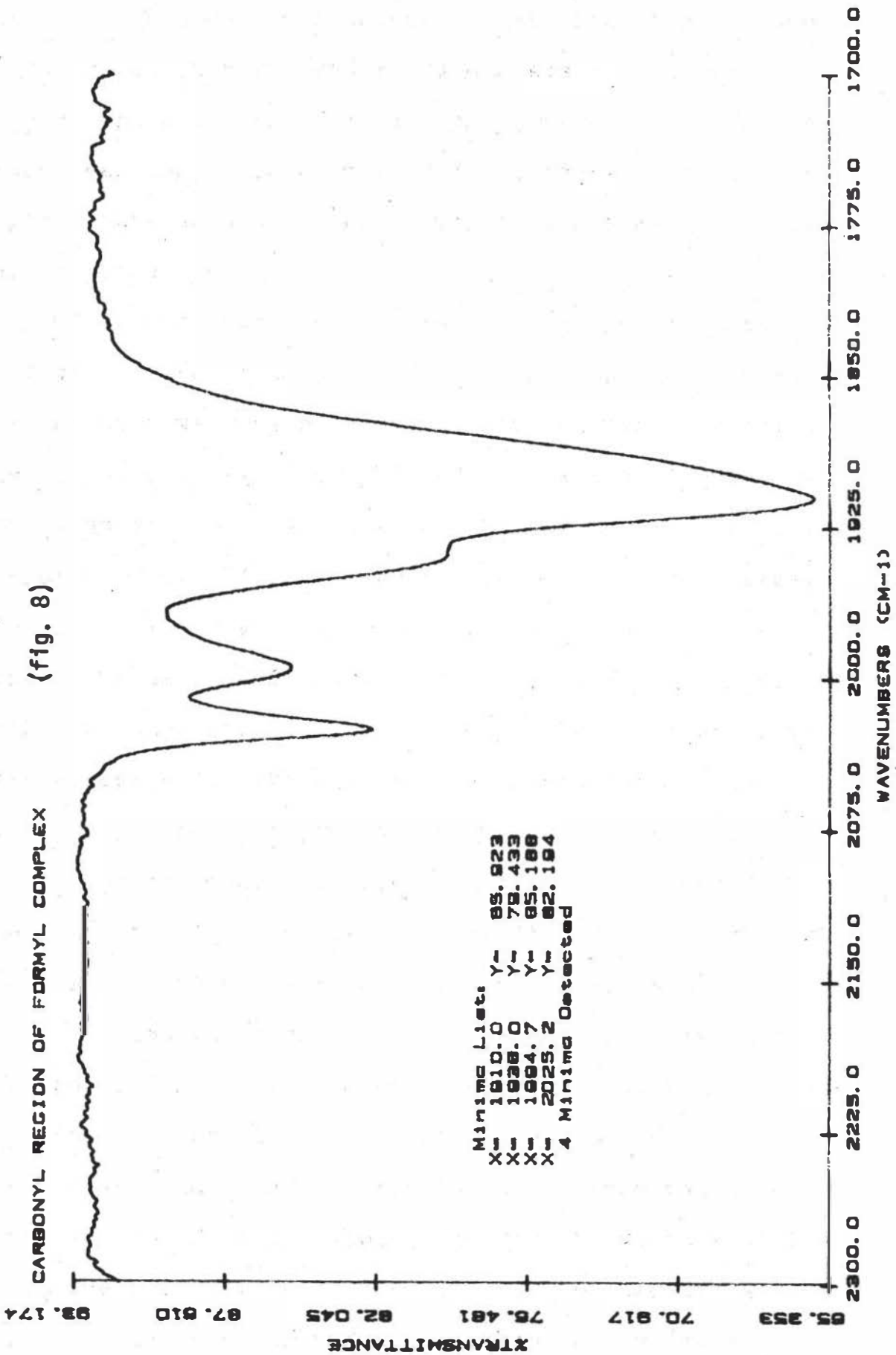
bers by 5 to 8 cm^{-1} was observed. At this point it should be indicated that at 1994.7 wavenumbers a peak was observed, which increased in intensity upon sitting of the crude reaction mixture at room temperature. An attempt to explain this absorption band will be undertaken in a later part of this paper.

After the detection of the carbonyl absorptions of the tetracarbonylformyliron(0) anion in the crude reaction mixture efforts were made to confirm the initial formation of the formyl complex. For this purpose a reaction was performed under the conditions as outlined in chapter II.2.2.2 Preparation of $(P(C_6H_5)_3)_2N^+(CO)_4Fe(CHO)^-$. This preparation is in close analogy with a preparation reported by Winter, Cornett, and Thompson in 1977[23], who reported the preparation of the bis(triphenylphosphine)iminium tetracarbonylformyliron(0) salt in THF and subsequent recrystallization of the salt from a mixture of dichloromethane and ether over the course of seven days in a 50 % yield. Even though obtaining crystals of the salt was not accomplished, clear spectroscopic evidence of the formation of the desired species was obtained. Below a spectrum is shown labeled as "PPN(CHO)Fe(CO)4" (fig. 9). This spectrum was obtained in dichloromethane from the dried residue after the solvent had been stripped from the crude reaction mixture. The sample dissolved in dichloromethane gave a clear and slightly yellow solution. The spectrum was recorded in a sodium chloride cell as described earlier. In

61

PPN (CHO) Fe (CO) 4   (fig. 9)

Minima List:
X= 1590.1   Y= 48.920
X= 1688.1   Y= 3.6426
X= 2015.0   Y= 48.984
3 Minima Detected
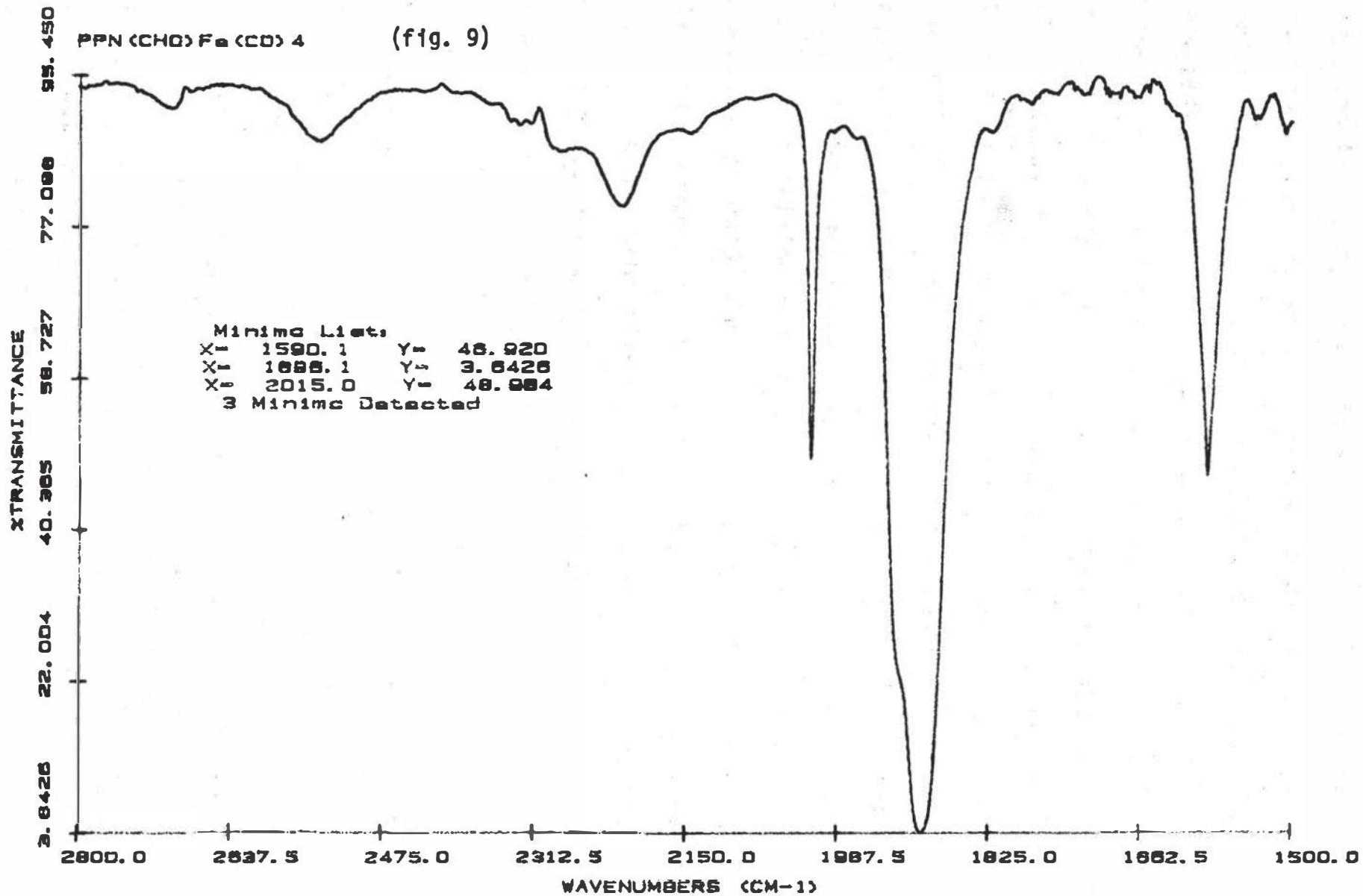
comparing the latter spectrum with the spectra of the crude reaction mixture shown earlier one notes that the carbonyl regions show the same absorption pattern. Furthermore, an absorption of medium intensity is observed at 1590.1 wavenumbers in the spectrum of the bis(triphenylphosphine)-iminium salt, which is due to the C=O stretching mode of the formyl ligand. In this place it should be noted that the absorption frequency of the formyl IR band is strongly dependent on the kind of cation interacting with the formyl oxygen. The extent of ion pairing between cation and formyl complex determines the absorption frequency, with tighter ion pairing resulting in lower frequencies, due to a decrease in bond order between the carbon and oxygen in the formyl group. The pairing of the cation through the formyl oxygen can be illustrated as shown in scheme III, with lower frequencies resulting from greater ion pairing as a function of the size of the cation.[23]

Scheme III

Cat^+

$$|O|$$
$$\|$$
$$H-C-Fe(CO)_4^-$$

A

$$Cat-O|$$
$$\|$$
$$H-C-Fe(CO)_4$$
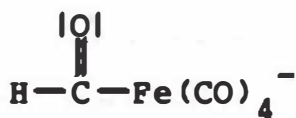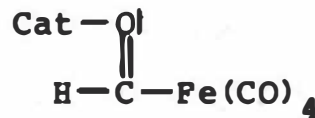
B

Cat^+ = cation

The contribution of B is increacing with greater ion pairing in the order $Li^+>Na^+>K^+>PPN^+$ as the cation. The shift in the absorption band for different counterions was found to cover a range of ca. 50 wavenumbers in spectra taken in THF.[23, 35] From the above discussion it becomes apparent that not only cations would influence the absorption frequency, but also Lewis acids and polar solvents would cause a shift in the absorption frequency of the formyl group. Considering the use of dichloromethane and 1-butanol, which is capable of hydrogen bonding with formyl oxygen, and the presence of various boron compounds in the solution used to obtain the spectra of the crude reaction mixture, it can be seen that the formyl group is the target of a number of various kinds of interactions. Due to these various interactions the signal of the formyl group in the infrared spectrum might be broadened considerably and its intensity delocalized over a wide range of wavenumbers. This would explain the observation made in spectra taken of the crude reaction mixture. In these spectra no peak was observed in the region where the formyl peak was expected. However, a rather broad absorption band of low intensity was observed in the proper region of the infrared spectrum. In order to illustrate the above discussion the spectra under investigation have been overlayed and are shown below labeled as "COMPARISON: FORMYL COMPLEX IN DIFFERENT ENVIRONMENTS" (fig. 10). Besides the absorptions mentioned above the formyl complex should exhibit

COMPARISON: FORMYL COMPLEX IN DIFFERENT ENVIRONMENTS   (fig. 10)

PPN((CHO)Fe(CO)$_4$) in dichloromethane

Na((CHO)Fe(CO)$_4$) from crude reaction mixture in dichloromethane
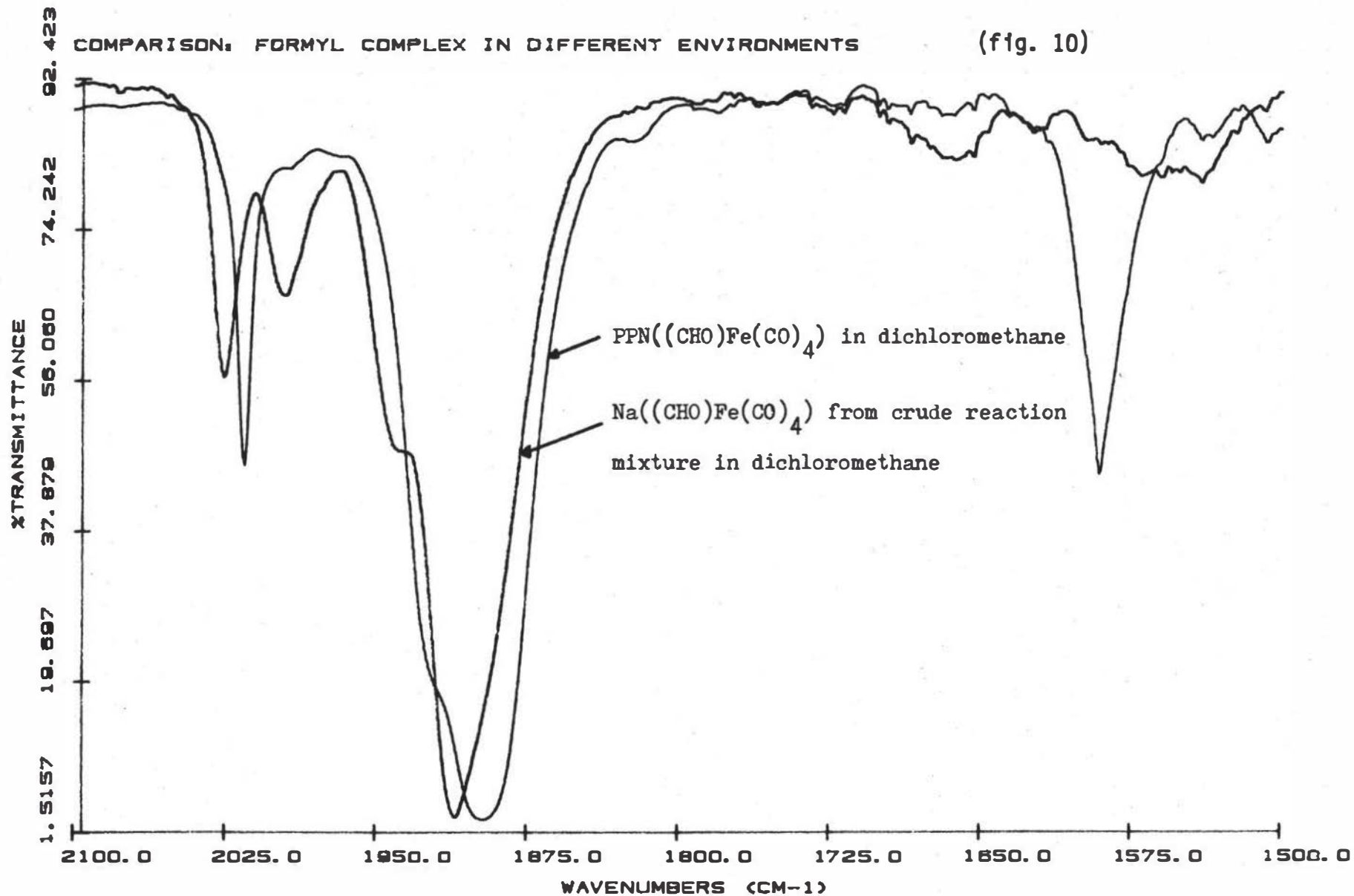
C-H vibrations of low intensity between 2830 and 2695 cm^{-1}. However, these absorption bands are not intense enough to be diagnostic.[36] As can be seen from the spectrum labeled as "PPN(CHO)Fe(CO)4" (fig. 9) two broad absorptions of low intensity, at 2701.0 and 2541.0 cm^{-1}, were observed. These absorption bands could not be unequivocally identified in spectra obtained from the crude reaction mixture.

Besides infrared spectroscopy, ^{1}H NMR spectroscopy was used to identify the iron formyl complex. For this purpose an experiment was performed as described in the experimental section of this paper under II.2.2.3. The spectrum which was taken about 30 minutes after the addition of iron pentacarbonyl, with the crude reaction mixture still at room temperature, is shown below labeled as "^{1}H NMR SPECTRUM OF $(CO)_4Fe(CHO)^-$" (fig. 11). In taking this spectrum benzene was used as an internal standard. A strong single peak shifted downfield of the benzene signal by 7.45 ppm was observed, giving a chemical shift of 14.65 ppm with respect to TMS. This value for the chemical shift is in good agreement with other values of the formyl proton found in the literature.[23, 24]

From the above discussion it is apparent that the formation of the tetracarbonylformylferrate(0) anion is the initial step in the reaction under investigation. Since the infrared spectra shown above were obtained by taking samples from homogeneous solutions, and since no spectroscopic evidence for the presence of iron pentacarbonyl was

^{1}H-NMR SPECTRUM OF (CO)Fe(CHO)$^-$ (fig. 11)

14.65 $\pm$ 0.1 ppm
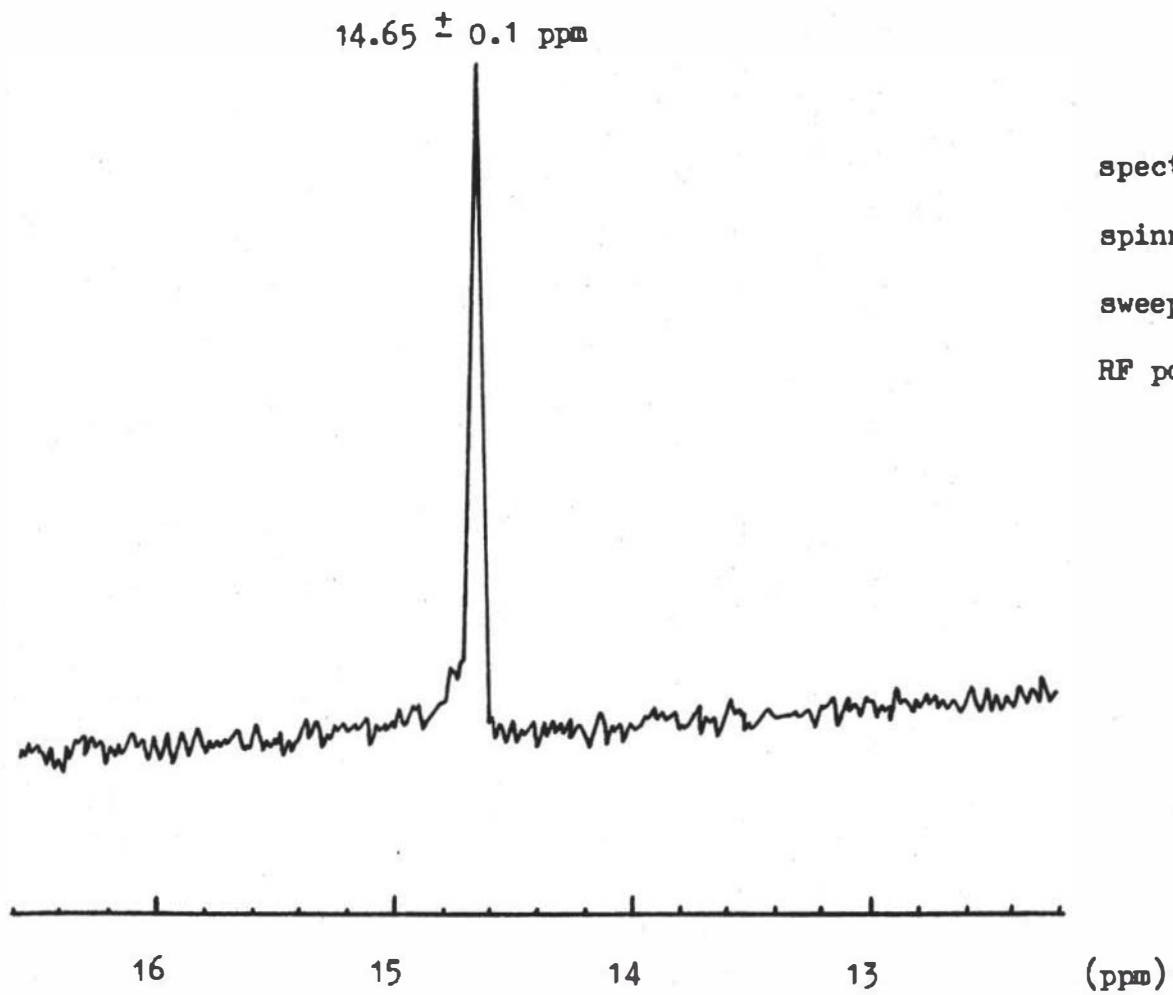
spectrum amplitude: 100

spinning rate (RPS): 44

sweep time (SEC):   250

RF power level: 0.05

16   15   14   13   (ppm)

observed in these spectra, it is concluded that the iron pentacarbonyl is quantitatively converted to the formyl complex by its interaction with the large excess of reducing agent. The presence of iron pentacarbonyl would result in two strong absorptions at 2020 (sh) and 1996 (vs) cm^{-1} as determined in 1:20 water/1-butanol.[37] Considering the information discussed above, as well as points outlined under III.3.3.1 Investigation of the Origin of the H_2 Gas, the mechanism for the formation of the formyl complex as shown below in scheme IV (fig. 12) is proposed. This mechanism is in close analogy with a mechanism proposed for the reduction of ketones in alcoholic solvents.[47] The proposed reaction sequence does not only account for the formation of the iron formyl complex, but also leads to the formation of hydrogen gas as well as a reactive boron compound, which is capable of releasing more hydrogen gas by reacting with the solvent.

68

$$BuOH \ + \ BH_4^- \ + \ Fe(CO)_5$$

$$Bu-\overline{O}-BH_2 \ + \ H_2$$
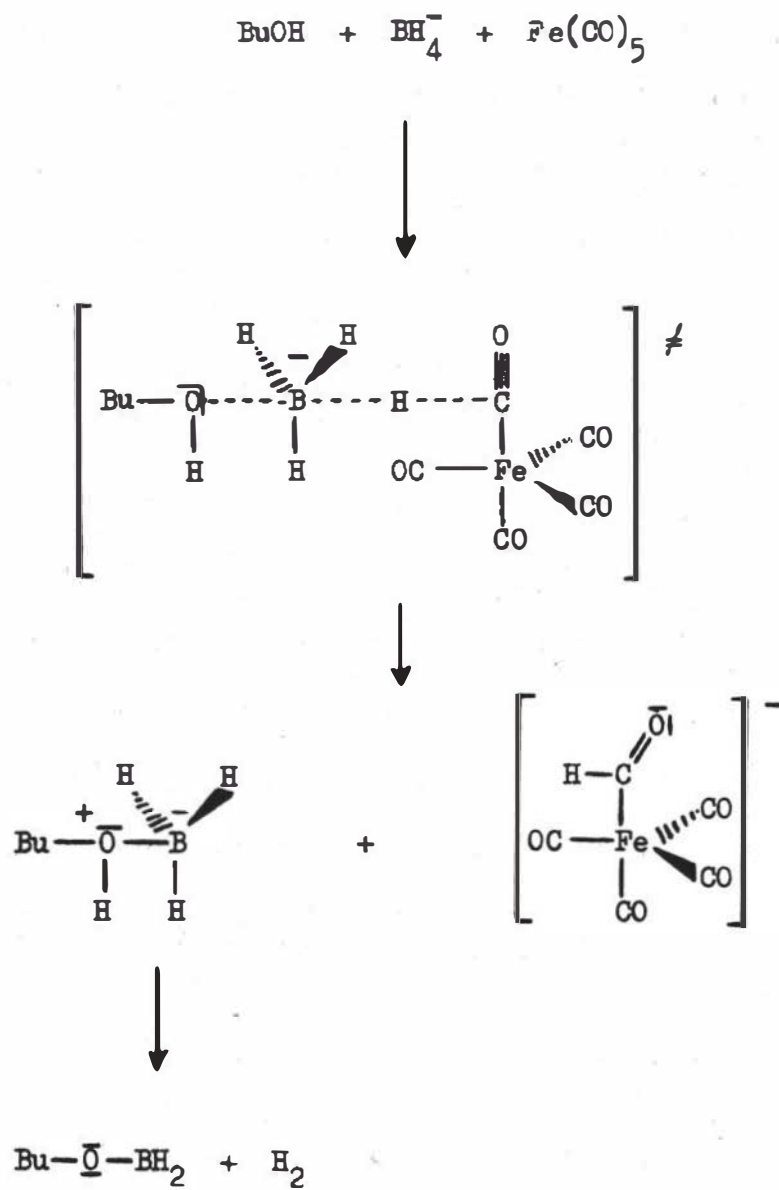
2.2 Thermally Facilitated Hydride Migration

Iron formyl complexes have been shown to typically decompose by loss of carbon monoxide. For instance, Collman and Winter reported that $Na[(CO)_4FeH]$ underwent slow decarbonylation to $Na[(CO)_4FeH]$ ($t_{1/2}$, 25 $^{\circ}$C, THF,> 12 days).[35] They also pointed out that no apparent decarbonylation took place in the solid state under reduced pressure (0.2 mm) at 25 $^{\circ}$C over a period of 13 days. This indicates that the stability of the formyl complex can be influenced essentially. Considering the conditions of the reaction under investigation, reflux temperature of 1-butanol, carbon monoxide loss of the formyl complex becomes a likely reaction, which leads to the formation of a monohydrido iron complex after hydride migration. Thus, it was expected to observe the tetracarbonylhydridoferrate(0) anion in the crude reaction mixture.

First hints on the decomposition of the tetracarbonylformylferrate(0) anion in the crude reaction mixture were obtained by means of infrared spectroscopy. The spectrum shown below, which is labeled as "MIXTURE: FORMYLIRON TETRACARBONYL ANION/HYDRIDOIRON TETRACARBONYL ANION" (fig. 13), was obtained by diluting a sample of the crude reaction mixture, which was taken about one hour after iron pentacarbonyl was added, at room temperature, in the absence of ligand, with a fivefold excess of chloroform. The presence of the hyrido species is concluded from the peak

MIXTURE: FORMYLIRON TETRACARBONYL ANION/ HYDRIDOIRON TETRACARBONYL ANION (fig. 13)

%TRANSMITTANCE

85.402
79.051
69.701
57.351
46.000
35.650

Minima List:
X= 1857.7   Y= 69.023
X= 1888.8   Y= 47.523
X= 1913.6   Y= 39.338
X= 1940.7   Y= 60.830
X= 1944.9   Y= 60.879
X= 1990.4   Y= 75.589
X= 2001.9   Y= 73.491
X= 2027.6   Y= 83.663
    8 Minima Detected

2200.0   2137.5   2075.0   2012.5   1950.0   1887.5   1825.0   1762.5   1700.0
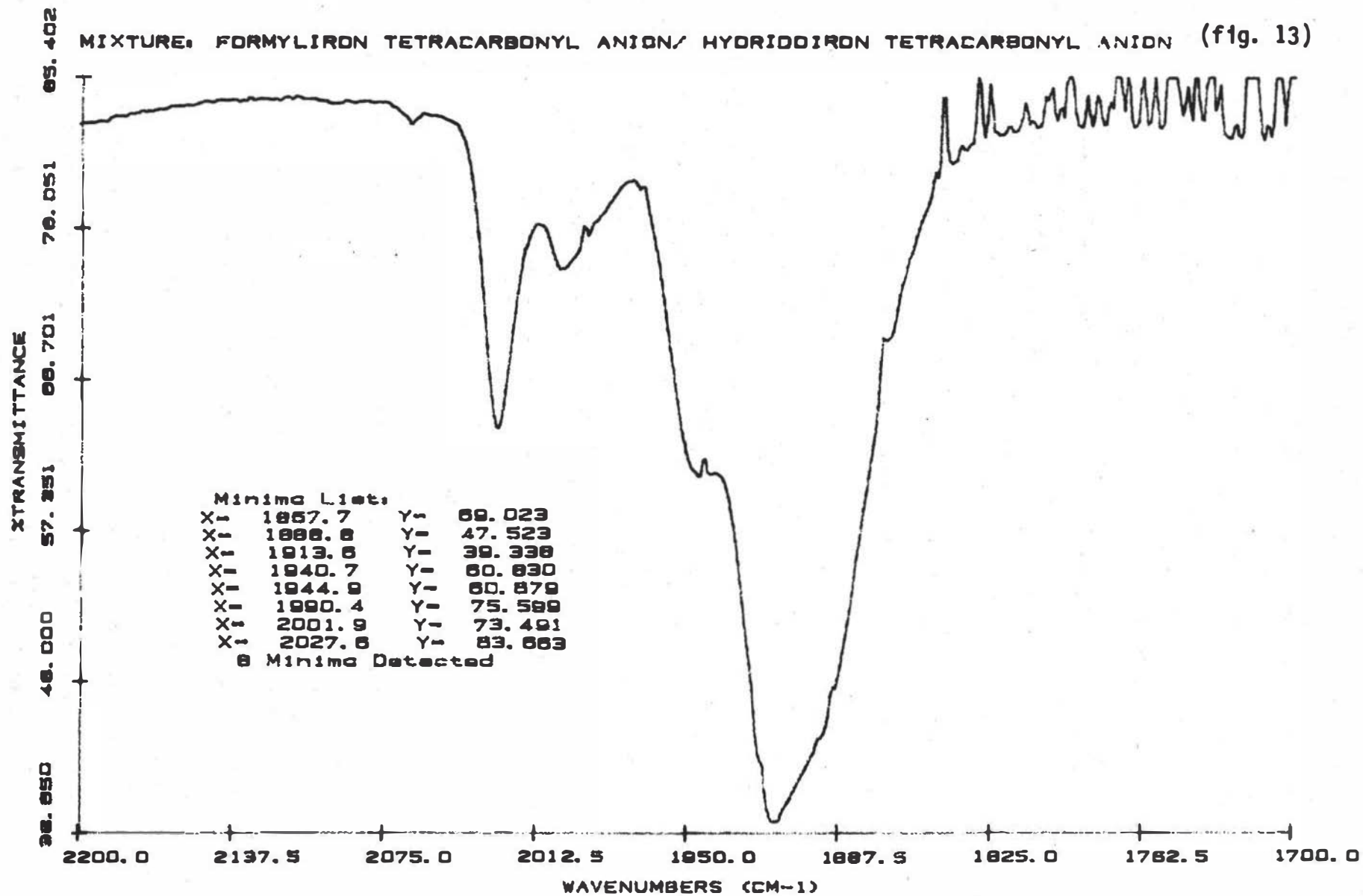
WAVENUMBERS (CM-1)

observed at 1867.7 cm^{-1} as well as the broadening of the most intense formyl peak to lower wavenumbers. A band at 2001.8 wavenumbers could be assigned to the $A_1^{(2)}$ vibrational mode. However, the intensity of that band seems too high to be the sole result of that vibrational mode (reported carbonyl stretching frequencies: 2008 (w), 1914 (m), 1880 (s) in dimethylformamide[38]; 1915 (s,sh), 1885 (vs), 1865 (sh) in a 1:20 mixture of water and 1-butanol[37]; 2008 (wm), 1910 (sh), 1848 (s,br) - mull[39]). From the reported stretching frequencies it is apparent that the absorption pattern and frequencies exhibited by the hydrido species strongly depend on the chosen conditions under which the spectrum of the anion is recorded. Valuable information about the intensities of CO stretching vibrational modes as well as their absorption pattern under varying conditions was obtained from a paper reported by M. Y. Darensbourg, D. J. Darensbourg, and H. L. C. Barros.[40] These workers showed that due to the C_{3v} symmetry of the $Fe(CO)_4$ moiety a rather simple spectrum is obtained for $(PPN)(HFe(CO)_4)$ in THF giving rise to three bands, which are assigned, in decreasing frequency, to the $A_1^{(2)}$ (1997.6 vw), $A_1^{(1)}$ (1904.7 m), and E (1875.8 s) vibrational modes. The above workers also investigated the more complex infrared spectrum which is obtained from the sodium salt of the tetracarbonyl-hydridoferrate(0) anion in THF. The sodium salt exists as a contact-species in solution, with a sodium ion interacting with one of the equatorial carbonyl oxygen atoms.

72

The interaction of the sodium ion with one of the carbonyl groups causes a lowering of the symmetry of the hydrido species and results in the observation of four absorptions in the infrared spectrum. A line drawing of the assignments of bands (2003, 1910, 1890, and 1854 cm^{-1}) as given by Darensbourg, Darensbourg, and Barros is shown below, labeled as "$(Na^+)(HFe(CO)_4^-)$ CONTACT-ION" (fig. 14). It should be noted that the intensity of the absorption at ca. 2000 wavenumbers has increased. For the purpose of comparison the absorptions of the $(PPN)(HFe(CO)_4)$ species taken in THF are given as dashed lines. From the above discussion it is seen that the presence of the $HFe(CO)_4^-$ ion in equilibrium with the $(Na^+...^-OC-Fe(CO)_3H)$ ion-pair gives rise to a more complex spectrum than initially expected. Considering the presence of a large amount of sodium ions in the crude reaction mixture ($Na^+:Fe = 4:1$) the spectrum labeled as "MIXTURE: FORMYLIRON TETRACARBONYL ANION/HYDRIDOIRON TETRACARBONYL ANION" (fig. 13) becomes more understandable. Further significant complication of the spectrum obtained by species such as Na_2A^+) and (Na_3A^{2+}), where A^- stands for the hydrido anion, are considered unlikely at the given concentration level.[40, 41]

In conclusion, the spectrum under investigation can be viewed as representing a mixture of the formyl complex, the concentration of which is still considerable as concluded from the intensity of the peak at 2027.6 cm^{-1}, and the two different forms of the tetracarbonylformylferrate(0) anion.

$(Na^+)(HFe(CO)_4{}^-)$ CONTACT-ION

(fig. 14)

$\bigast$ = $CO \cdots Na^+$

$\bullet$ = H

$\bigcirc$ = CO

ABSORBANCE

$(CM-1)$

74
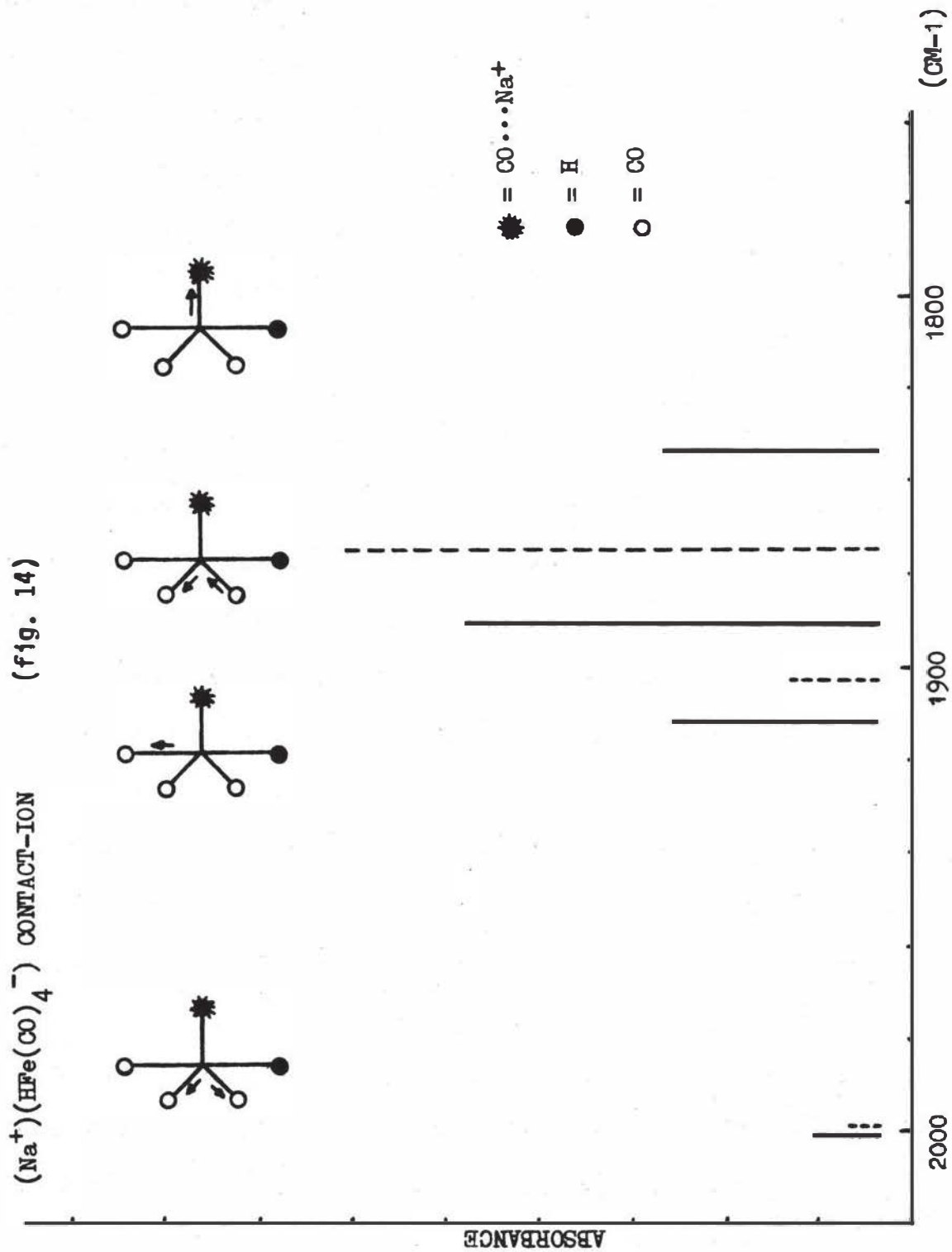
Hence, it indicates the decomposition of the formyl complex to yield the hydrido species. An earlier hint that the above conversion takes place was obtained by analysing the gas which forms immediately after the addition of iron pentacarbonyl to the solution of sodium borohydride in 1-butanol. In the analysis of the gas, which is described in part 3 of this chapter, traces of carbon monoxide were detected. The evolution of this gas is thought to be caused by the decomposition of the formyl complex.

In the hope to observe a quantitative conversion of the formyl complex an experiment was performed as described in the experimental section in this paper under II.2.2.1 Reaction of $Fe(CO)_5$ with PPh_3 in a 1:1 Ratio. A spectrum which was obtained from a sample taken immediately after the crude reaction mixture reached reflux is shown below labeled as "CRUDE REACTION MIXTURE AT REFLUX IN THE ABSENCE OF LIGAND" (fig. 15). From the peaks at 2024.5 and 2000.8 wavenumbers the presence of both the formyl and the hydrido complex is concluded. Due to the presence of these two complexes, the most intense peaks of these compounds overlap to give a very broad band between approximately 1960 and 1840 wavenumbers. A spectrum taken after a reflux period of 15 minutes is also shown below labeled as "CRUDE REACTION MIXTURE AFTER 15 MINUTES OF REFLUX IN THE ABSENCE OF LIGAND" (fig. 16). From that spectrum it can be seen that the formyl peak at 2025 wavenumbers disappeared leaving a peak at ca. 2000 wavenumbers as well as an in

75

CRUDE REACTION MIXTURE AT REFLUX IN THE ABSENCE OF LIGAND   (fig. 15)

Minima List:
X=   1897.8   Y=   26.772
X=   2000.8   Y=   55.550
X=   2024.5   Y=   58.231
    3 Minima Detected

%TRANSMITTANCE

WAVENUMBERS (CM-1)

76

(fig. 16)

CRUDE REACTION MIXTURE AFTER 15 MINUTES OF REFLUX IN THE ABSENCE OF LIGAND

Minima List:
X= 1710.6   Y= 43.790
X= 1894.7   Y= 35.831
X= 2002.7   Y= 59.254
  3 Minima Detected

SHOULDER AT CA. 1920 (CM-1)

SHOULDER AT CA. 1875 (CM-1)

%TRANSMITTANCE

WAVENUMBERS (CM-1)

77

tense peak at 1894.7 cm^{-1} having shoulders to both lower and higher wavenumbers. Observations made by means of infrared spectroscopy of the kind discussed above provided the initial evidence for the conversion of the formyl complex to form the tetracarbonylhydridoferrate(0) anion. A striking feature of the last spectrum shown is a strong absorption at 1710.6 cm^{-1}. This peak is due to the presence of the dianion Fe(CO)$_4^{2-}$. Only traces of this species were observed in some of the crude reaction mixtures to which the ligand had been added prior to heating. In the present case its formation can be rationalized by deprotonation of the tetracarbonylhydridoferrate(0) anion by excess reducing agent.[23]

In order to obtain more conclusive evidence for the thermal instability of the formyl species an ^{1}H NMR experiment was performed as outlined under II.2.2.3 (CO)$_4$Fe(HCO)$^-$ - Decomposition (^{1}H NMR Experiment). The first ^{1}H NMR spectrum which was recorded approximately 30 minutes after the iron pentacarbonyl had been added showed the formyl complex only and was discussed earlier. The second spectrum was taken after the crude reaction mixture had been sitting at room temperature for ca. one day and after a period of heating (30 min, 70 ^{o}C). This spectrum showed the presence of formyl complex as well as the hydrido complex. After an additional period of sitting and a period of heating (1 hr) the last ^{1}H NMR spectrum was taken which showed the presence of the formyl complex only. A

chemical shift of − 9.9 +/− 0.1 ppm relative to TMS was
determined using benzene as an internal standard. In the
literature a chemical shift relative to TMS of − 8.74 ppm
is reported.[42] Even though the reported chemical shift of
the hydride in the dinuclear anion $HFe_2(CO)_8^-$ of − 8.47
$ppm^{[42]}$ is very close to the one reported for the mononuclear
hydride, the dinuclear hydride can be excluded since in not
a single case of the recorded infrared spectra was evidence
obtained for the presence of bridging carbonyls. Carbonyls
coordinated to two or more metals would result in charac-
teristic absorption bands at wavenumbers well below those
observed. Thus, the participation of the dinuclear as well
as other polynuclear iron carbonyl hydrides can be ex-
cluded. The latter would exhibit chemical shifts relative
to TMS of at least 5 ppm further upfield.[25] The spectrum
of the tetracarbonylhydridoferrate(0) anion is given below
labeled as "^1H NMR SPECTRUM OF $HFe(CO)_4^-$" (fig. 17).

So far it has been shown that the iron formyl species
is not stable under the conditions in the crude reaction
mixture and decomposes to form a mononuclear iron carbonyl
hydride. This process seems to occur only slowly at room
temperature. However, upon heating the decomposition is
significantly enhanced. At this point it should be empha-
sized that the conversion of the formyl complex to form the
hydrido species is irreversible.[36, 43] From the observa-
tions made and by comparison with the literature[36] it
appears that the formyl complex decomposes by a rather

^{1}H-NMR SPECTRUM OF HFe(CO)$_4^-$ (fig. 17)

- 9.93 $\pm$ 0.1 ppm
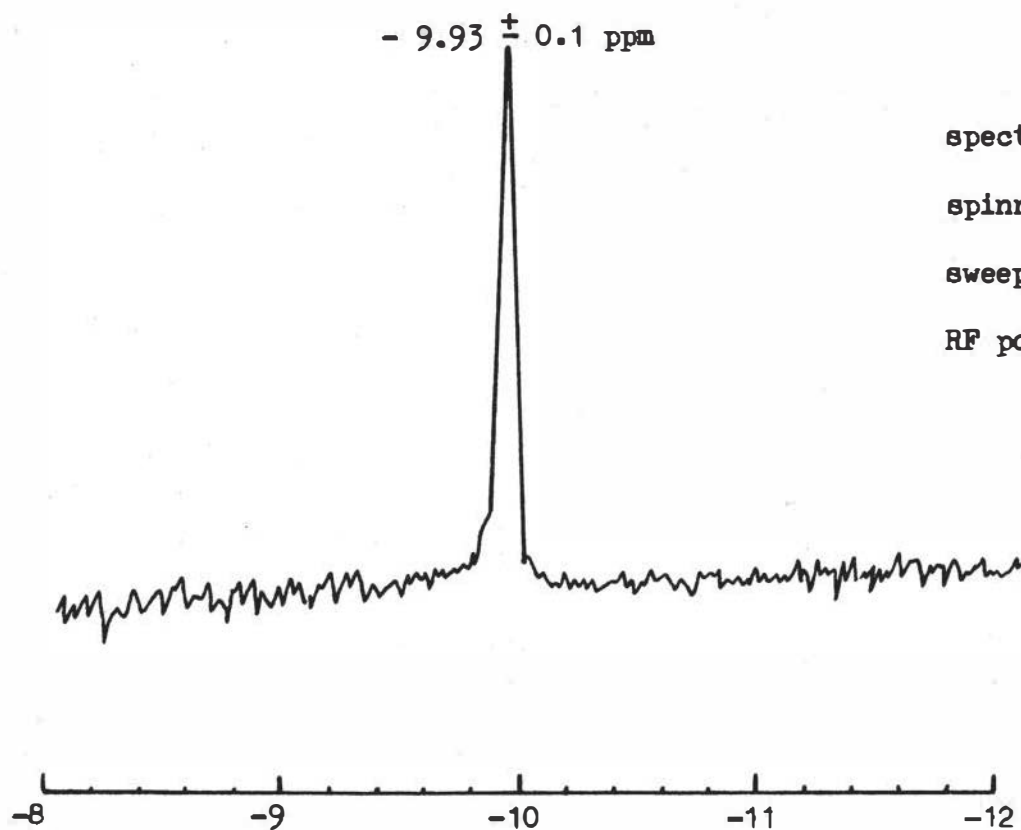
spectrum amplitude: 100

spinning rate (RPS):   40

sweep time(SEC):   250

RF power level: 0.05

simple pathway, with the loss of carbon monoxide being the rate determining step. This seems to be in good agreement with the observed temperature dependence of the formation of the $HFe(CO)_4^-$ complex. The initial loss of coordinated carbon monoxide is then followed by a rapid hydride migration to the central atom.

2.3 Reactivity of Tetracarbonylhydridoferrate(0)

It has been shown that in the initial step of the reaction mechanism the tetracarbonylformylferrate(0) anion forms which converts into the tetracarbonylhydridoferrate(0) anion by carbon monoxide loss and subsequent rapid hydride migration. From the literature it was not possible to find a single case in which the reaction of a nucleophile with the tetracarbonylhydridoferrate(0) was described. The contrary was found to be the truth. Walter O. Siegl reported in 1975 that the treatment of $HFe(CO)_4^-$ with $P(CH_2CH_2CN)_3$ in THF for 2.5 days in a 75 $^\circ$C oil bath did not result in any changes in the carbonyl region of the infrared spectrum. Subsequent addition of $LiAlH_4$ and another 2.5 days of heating still did not result in a reaction.[22] Unfortunately it was not reported whether decomposition of the iron complex occurred under the reaction conditions or not. The tetracarbonylhydridoferrate(0) anion has been proved to be unreactive in THF; however, its reactivity in 1-butanol is evidenced by the formation of trans-disubstituted iron tricarbonyl complexes in good to very good yields.

Even though the potential of the hydrido complex to form the trans-substituted products has not been proved with last certainty, observations have been made which strongly suggest that the hydrido species is a precursor for the obtained products. Convincing evidence for the

hydrido complex to play an important role in the reaction mechanism was obtained by means of IR spectroscopy from a reaction which was first run over an extended period of time at room temperature and then heated to reflux. The starting conditions for that reaction were identical with those described for other preparations of the disubstituted product. The crude reaction mixture, which contained sodium borohydride, iron pentacarbonyl, and triphenylphosphine in 1-butanol, was stirred at room temperature for ca. 10 days and monitored by IR spectroscopy. A sequence of spectra taken from the crude reaction mixture is shown below. The spectra are labeled as: "CRUDE REACTION MIXTURE AT ROOM TEMPERATURE AFTER ONE DAY" (fig. 18) and "CRUDE REACTION MIXTURE AT ROOM TEMPERATURE AFTER TEN DAYS" (fig. 19) as well as "CRUDE REACTION MIXTURE AFTER 30 MINUTES OF REFLUX" (fig. 20). The first of these spectra shows a rather complex absorption pattern in the carbonyl region of the IR spectrum. For simplicity the assumption shall be stated, but not discussed, that the given spectrum represents a mixture of the formyl and hydrido anions, which have been discussed earlier, as well as monosubstituted product. The presence of the latter is concluded due to the absorption band at 2050.1 cm^{-1}. A remarkable change in the composition of the reaction mixture took place during an additional nine days of stirring under nitrogen as can be seen from the second IR spectrum shown. The most intense absorptions in the region between

83

CRUDE REACTION MIXTURE AT ROOM TEMPERATURE AFTER ONE DAY   (fig. 18)

84

Minima List:
X=   1892.1   Y=   61.808
X=   1912.7   Y=   63.994
X=   1942.9   Y=   73.828
X=   1989.7   Y=   68.528
X=   2024.1   Y=   67.962
X=   2050.1   Y=   80.900
6 Minima Detected

CRUDE REACTION MIXTURE AT ROOM TEMPERATURE AFTER TEN DAYS   (fig. 19)

Minima List:
X=   1887.0   Y=   53.841
X=   1936.4   Y=   75.763
X=   1974.9   Y=   91.389
X=   1994.1   Y=   91.841
X=   1998.0   Y=   92.127
X=   2024.8   Y=   90.040
X=   2049.9   Y=   88.178
   7 Minima Detected

Shoulder at ca. 1907 cm-1

%TRANSMITTANCE

WAVENUMBERS (CM-1)

CRUDE REACTION MIXTURE AFTER 30 MINUTES OF REFLUX   (fig. 20)

Minima List:
X= 1885.8   Y= 14.348
X= 1918.0   Y= 59.233
X= 1935.9   Y= 64.003
X= 1974.8   Y= 65.443
X= 2004.1   Y= 83.485
X= 2049.9   Y= 75.469
6 Minima Detected

98

approximately 1860 and 1950 cm^{-1} as well as the absorption band at ca. 2000 cm^{-1} clearly stand for the tetracarbonyl-hydridoferrate(0) anion and the corresponding contact-ion. The spectrum resulting from a mixture of these two species has been outlined in detail earlier. It should also be noted that the absorption frequencies for the $A_1^{(1)}$ and E mode are shifted to higher wavenumbers by approximately 12 cm^{-1} compared to the frequencies reported by Darensbourg, Darensbourg, and Barros[40], who recorded their spectra in THF. The bands of low intensity are assigned to the formyl complex, only the carbonyl vibrational band at 2024.8 cm^{-1} can be observed, since the other bands are covered by the intense hydride absorptions. The peaks at 2049.9 and 1974.6 cm^{-1} are assigned to the complex $Fe(CO)_4PPh_3$ (reported[5]: 2059, 1978, and 1938 cm^{-1} in chloroform with intensities of 3:3:10). The low frequency band of the monosubstituted product is thought to contribute to the strong shoulder at 1936.4 cm^{-1}. So far only the expected conversion of the formyl complex has been shown by the detection of the hydrido complex. At this point it should be noted that the crude reaction mixture did not show any signs of decomposition. The color of the solution was still yellow. Even though the solution was turbid, clear solutions were obtained upon mixing of the sample with chloroform, which was done to obtain a sufficiently dilute sample to take an IR spectrum.

After ten days at room temperature, which had caused

87

the formation of the hydrido species, the reaction mixture was heated to reflux for a period of 30 minutes. The IR spectrum which was taken after the solution had cooled down to room temperature is shown below labeled as "CRUDE REACTION MIXTURE AFTER 30 MINUTES OF REFLUX" (fig. 20). From the obtained spectrum it is obvious that the product of the reaction is a mixture of monosubstituted (2049.9, 1974.6, and 1935.9 cm^{-1}) and disubstituted (1885.8 cm^{-1}) triphenylphosphine derivatives of iron pentacarbonyl. However, the spectrum still showed a peak of low intensity at ca. 2000 wavenumbers. Thus, the presence of hydrido complex was assumed and the reaction mixture was heated to reflux for an additional hour, which caused the peak of interest to decrease, but not to vanish. The $Fe(CO)_3(PPh_3)_2$ complex was isolated in good yield from the crude reaction mixture by filtration and washing of the obtained residue with methanol. The product was identified by its IR absorption at 1885.3 cm^{-1} in chloroform and its decomposition point of 290 - 2 ^{o}C.

Even though it has been shown by infrared spectroscopy that after the formation of the tetracarbonylhydridoferrate(0) anion a rapid formation of the desired phosphine disubstituted product is achieved upon heating of the crude reaction mixture in the presence of ligand, it is understood that this is not a valid proof for the hydrido species being the precursor for the disubstituted product. Nevertheless, since all spectra were taken of clear,

apparently homogeneous solutions, which would give rise to spectra that give a complete picture of the composition of the reaction mixture, it is believed that the obtained spectra give reliable information about the conditions prevailing in the reaction mixture.

In the above context it shall also be pointed out that spectra obtained from reaction mixtures in the process of heating, prepared by the standard procedure described in the experimental part (method I, method II), showed absorptions which could possibly be assigned to the hydrido species. However, due to the presence of ligand not only absorptions of the formyl and hydrido complex contribute to the observed absorption pattern in the carbonyl region, but also product as well as contaminations of the monosubstituted derivative of iron pentacarbonyl further complicate the recorded spectra, thus, making unequivocal assignments of peaks almost impossible, especially in the present case, where all expected absorptions appear in a region with a width of ca. 200 wavenumbers, only. An example to demonstrate the complexity of the crude reaction mixture is given below labeled as "CRUDE REACTION MIXTURE" (fig. 21). The spectrum shown was taken before the reaction mixture reached reflux temperature. As outlined above, little information on the course of the reaction, especially after the formation of the hydrido complex, is obtained by monitoring the crude reaction mixture in time by IR spectroscopy.

CRUDE REACTION MIXTURE   (Fig. 21)

%TRANSMITTANCE vs WAVENUMBERS (CM-1)
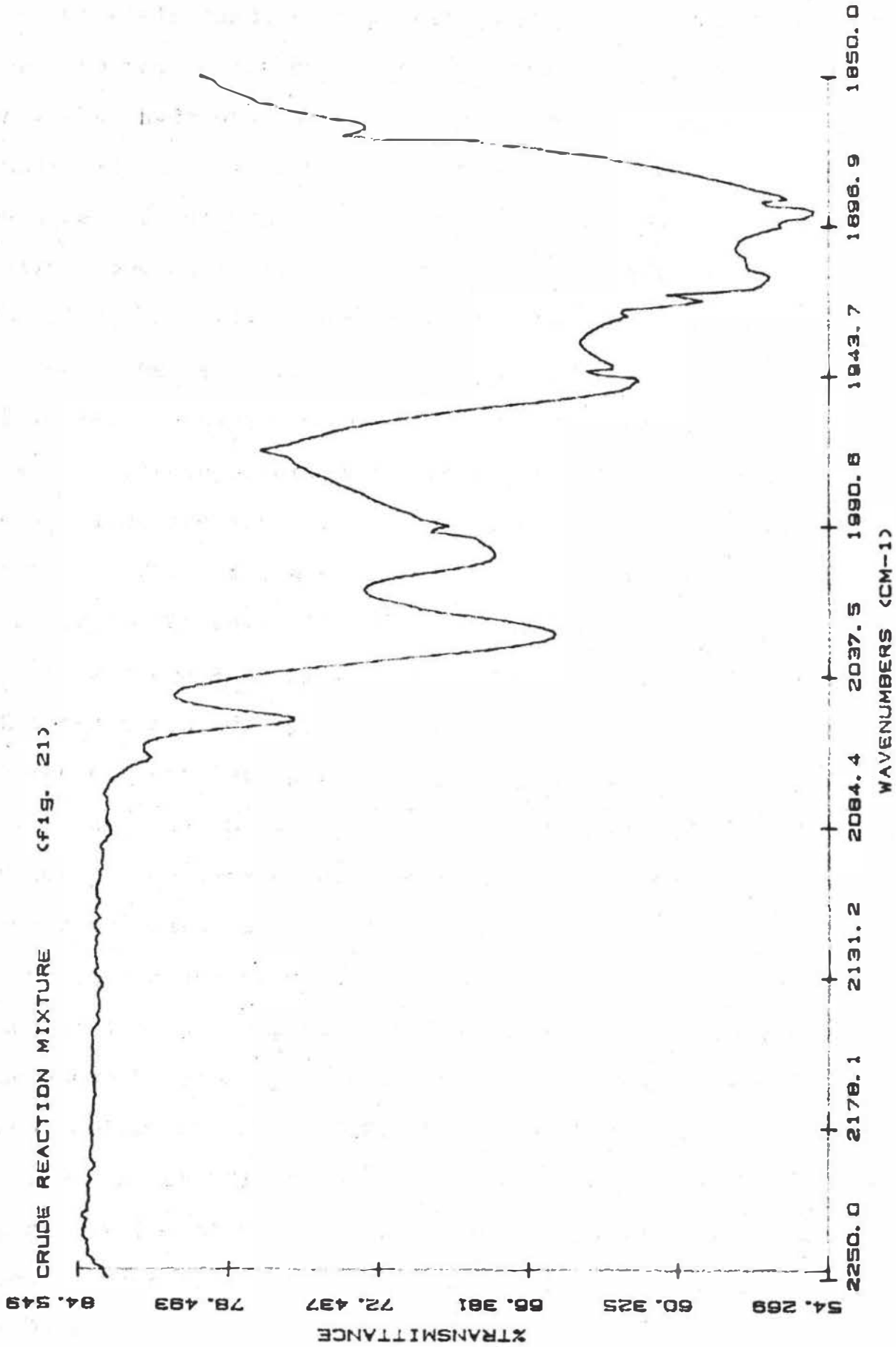
Of basic concern in investigating the mechanism that leads to the formation of $Fe(CO)_3(PR_3)_2$ complexes was to show that hydridoiron carbonyl complexes are capable of undergoing reactions with phosphines. This was necessary, because hydrido species have not been reported to be reactive towards substitution reactions. Under the above considerations reactions, were performed as described in the experimental part of this paper under II.2.2.4 Reaction of Tetracarbonylhydridoferrate(0). Unfortunately, not only the tetracarbonylhydridoferrate(0) was formed, but also polynuclear species formed under the given conditions. A spectrum taken of the collected THF extracts is given below labeled as "EXTRACT (THF)" (fig. 22). Even though the spectrum shows a complex absorption pattern, the presence of certain hydrido species can be concluded. With a high degree of certainty the two strong peaks at 1908.0 and 1878.1 cm^{-1} can be assigned to the mononuclear hydride $HFe(CO)_4^-$ (compare discussion of $HFe(CO)_4^-$ spectrum). All remaining peaks can be assigned to either the dinuclear or trinuclear monohydrido species.[39] A spectrum showing a similar absorption pattern was obtained from a mixture of the above hydrido species in 1-butanol. The spectrum is shown below labeled as "EXTRACT (BUTANOL)" (fig. 23). The strong peak at 1710.8 cm^{-1} is due to $Fe(CO)_4^{2-}$ and vanished after sitting of the 1-butanol extract under nitrogen over night. Both mixtures of hydrido species yielded disubstituted product in good yield after addition of ligand and re-

EXTRACT (THF)   (fig. 22)

Minima List:
X=   1748.8   Y=   75.461
X=   1779.0   Y=   69.499
X=   1878.1   Y=   1.8687
X=   1908.0   Y=   21.130
X=   1942.5   Y=   23.778
X=   1970.0   Y=   23.986
X=   1982.4   Y=   31.159
X=   1992.0   Y=   21.882
X=   1998.5   Y=   27.553
X=   2018.3   Y=   74.639
      10 Minima Detected

%TRANSMITTANCE

WAVENUMBERS (CM-1)

92

EXTRACT (BUTANOL)   (Fig. 23)

%TRANSMITTANCE

WAVENUMBERS (CM-1)
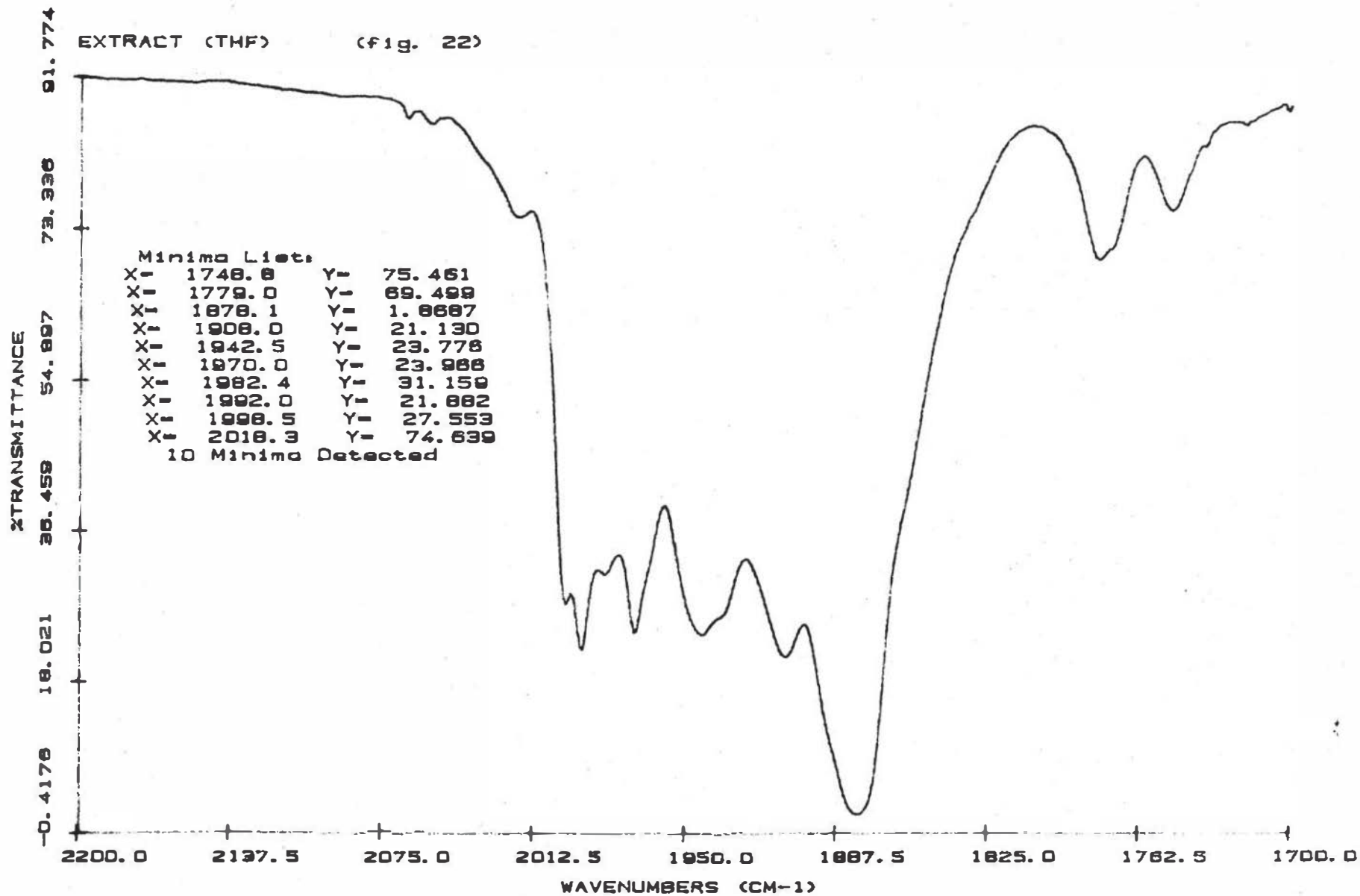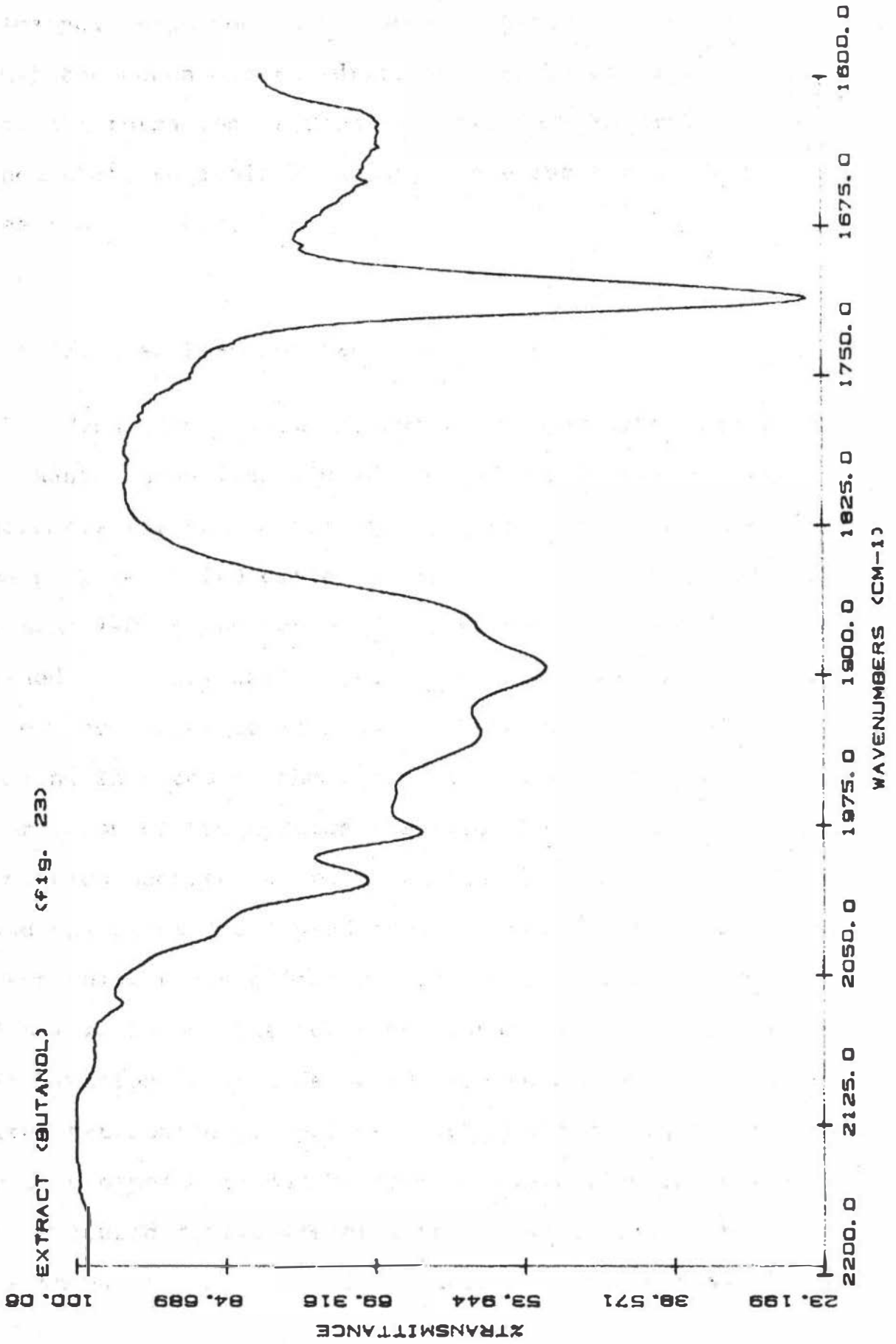
fluxing. Even though the above experiments do not prove that the mononuclear hydrido species is solely responsible for the formation of trans-substituted product, it does show that hydridoiron carbonyls are capable of forming the desired products.

2.4 Proposed Reaction Mechanism

Even though only the initial stages of the reaction mechanism have been elucidated, a complete mechanism, which accounts for the formation of disubstituted product, shall be proposed. The different steps of the mechanism are summarized in the scheme given below (fig. 24). As out-lined in detail earlier, the initially formed formyl complex decomposes to form the tetracarbonylhydridoferrate(0) anion. The step in the reaction mechanism following the formation of the hydride requires the supply of energy. No reaction occurred at room temperature between the hydride and the phosphine ligand as demonstrated previously. At this point three principle mechanistic steps can be imagined to account for a continuation of the reaction. Elimination of hydride would lead to a neutral 16-electron iron tetracarbonyl species which would undergo substitution with phosphine ligand to form a stable 18-electron mono-substituted derivative of iron pentacarbonyl. This route is thought to be possible to account for the small amounts of monosubstituted product detected in crude reaction

Proposed Mechanism for the Formation of $Fe(CO)_3(PR_3)_2$ (fig. 24)

a) $Fe(CO)_5 \xrightarrow[\substack{n-BuOH \\ room\ temp.}]{NaBH_4} (CO)_4Fe(CHO)^- Na^+ + BH_3$

b) $(CO)_4Fe(CHO)^- \xrightarrow[-\ CO]{heat} HFe(CO)_4^-$

c)

$$\left[\begin{array}{c} OC-Fe \overset{H}{\underset{CO}{\bigm|}} \overset{\cdots CO}{\diagdown CO} \end{array} \right]^- + PR_3 \xrightarrow[\substack{-\ CO \\ i)\ or\ ii)}]{heat} \left[\begin{array}{c} OC-Fe \overset{H}{\underset{PR_3}{\bigm|}} \overset{\cdots CO}{\diagdown CO} \end{array} \right]^-$$
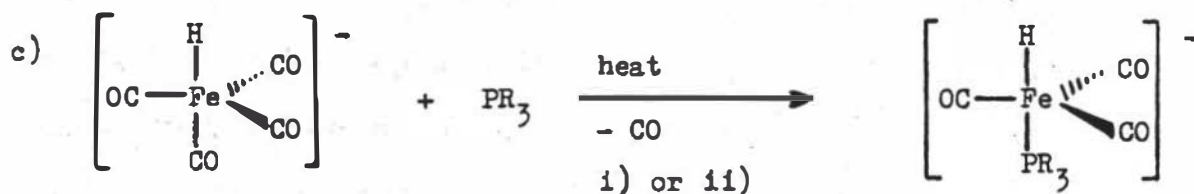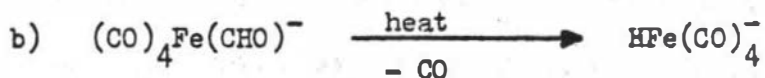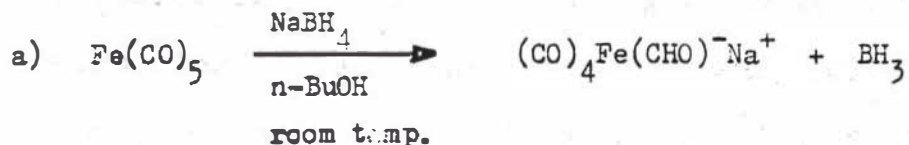
i) elimination of CO, addition of PR_3 (S_N1)

ii) direct replacement of the axial CO ligand by PR_3 (S_N2)

d)

$$\left[\begin{array}{c} OC - Fe \overset{H}{\underset{PR_3}{\bigm|}} \overset{\cdots CO}{\diagdown CO} \end{array} \right]^- + BuOH \longrightarrow H_2 + OC - Fe \overset{(OBu^-)}{\underset{PR_3}{\bigm|}} \overset{\cdots CO}{\diagdown CO}$$

e)

$$OC - Fe \overset{(OBu^-)}{\underset{PR_3}{\bigm|}} \overset{\cdots CO}{\diagdown CO} + PR_3 \longrightarrow OC - Fe \overset{PR_3}{\underset{PR_3}{\bigm|}} \overset{\cdots CO}{\diagdown CO}$$

$Fe(CO)_5 + 2\ PR_3 \xrightarrow{NaBH_4,\ heat} Fe(CO)_3(PR_3)_2 + 2\ CO$
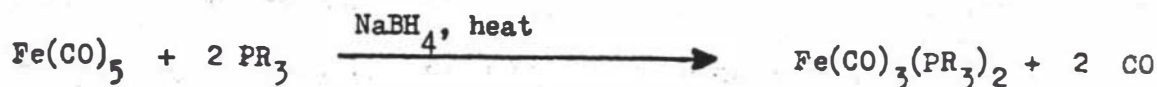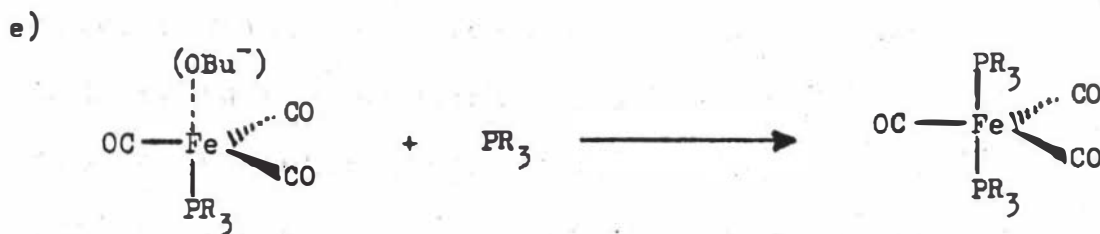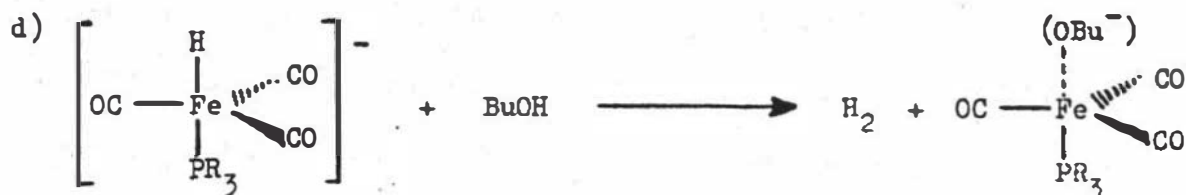
mixtures by IR spectroscopy. Even though monosubstituted
derivatives of iron pentacarbonyl are known to undergo
further substitution under thermal conditions[6] as well as
reducing conditions[22] this route can not account for the
formation of large amounts of disubstituted product under
the given conditions. Substitution of $Fe(CO)_4PR_3$ with a
second ligand has been shown to proceed only slowly giving
low yields, even if run over extended periods of time.[6, 22]
A second possible pathway would be a direct replacement of
one of the carbonyl ligands by phosphine in an S_N2 type of
substitution. Replacement of the hydride would result in
monosubstituted product and the problems which are outlined
above. However, this mechanism is quite unlikely con-
sidering the presence of filled d-orbitals (d_{xz}, d_{xy}, d_{yz},
$d_{x^2-y^2}$) which occupy the space between the ligands and
which would repell incoming ligands.

A mechanism which is believed to be most likely to
yield the disubstituted product involves the dissociation
of CO from the hydridoiron species. Iron carbonyls are
known to typically decompose by loss of coordinate carbon
monoxide (compare chapter I). Hence, a phosphine substi-
tuted hydridoiron tricarbonyl is postulated as an inter-
mediate in the proposed mechanism, which is thought to form
from a 16-electron hydridoiron tricarbonyl anion by substi-
tution with phosphine. Due to the phosphine substituent,
which is a worse pi-acceptor and better sigma-donor than
the carbonyl ligand, the electron density on the central

metal is increased compared to the unsubstituted hydrido species. The increase in electron density on the iron causes the hydrogen to be more hydridic. As a possible pathway that leads to the formation of disubstituted product after the formation of the postulated hydridoiron tricarbonyl phosphine intermediate the dissociation of a hydride seems to be likely. This step can either be caused by the high temperature or be facilitated by an interaction between the hydride and the alcoholic hydrogen. In both cases the result would be the formation of a 16-electron iron species as well as hydrogen gas as a side product. Coordination of 1-butanol or the formed butanolate anion appears reasonable; however is not essential for the course of the reaction. The important step is the participation of a 16-electron species which is readily substituted with phosphine in order to obtain the favorable configuration of 18 electrons in the outer orbitals of iron and thus, leading to the desired disubstituted product.

At this point it should be emphasized that the final steps of the mechanism have not been proved; however, besides the general considerations outlined above, observations have been made in the course of this work which are in agreement with the proposed final steps of the mechanism. A characteristic feature of the reaction under investigation is that only small amounts of monosubstituted product are formed. An example for the presence of small amounts of monosubstituted product in the crude reaction

CRUDE REACTION MIXTURE AFTER 3 HOURS OF REFLUX   (fig. 25)

Minima List:
X= 1886.2   Y= 45.272
X= 1940.2   Y= 87.709
X= 1970.4   Y= 92.393
X= 2050.3   Y= 97.484
  4 Minima Detected

86
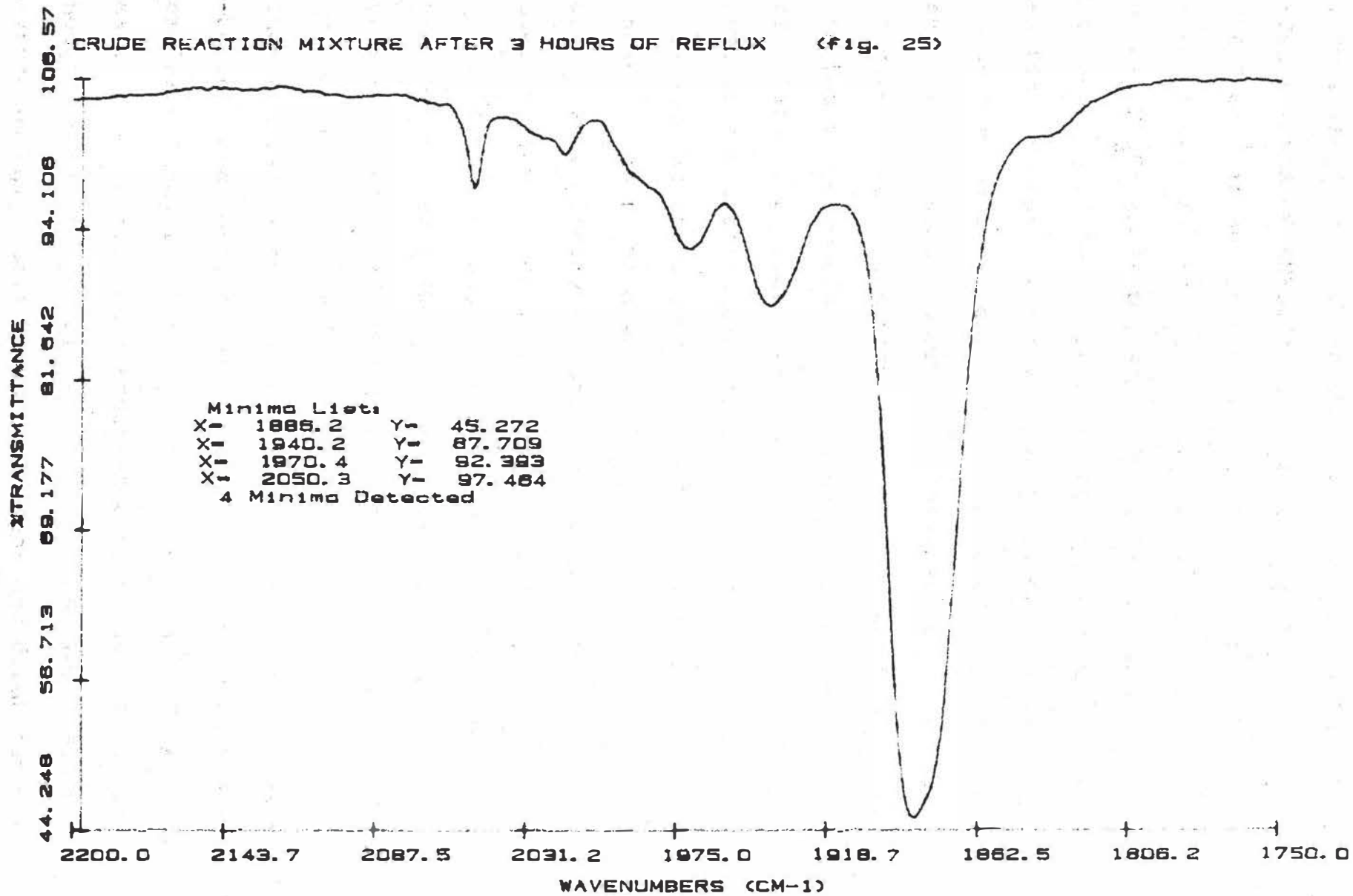
mixture is given below labeled as "CRUDE REACTION MIXTURE AFTER 3 HOURS OF REFLUX" (fig. 25). The strong peak at 1886.2 cm^{-1} is due to the complex $Fe(CO)_3(PPh_2CHCH_2)_2$, the peaks at 2050.3, 1970.4, and 1940.2 cm^{-1} are due to $Fe(CO)_4PPh_2CHCH_2$ (reported:[29] 2054, 1979, and 1946 cm^{-1}). The shown spectrum is in agreement with a number of expected features for a reaction that proceeds according to the proposed mechanism. For reasons outlined above the presence of only small amounts of monosubstituted derivative indicates that a mechanism other than a stepwise substitution has to be considered. Furthermore, the fact that the disubstituted product is already present in large amounts requires a mechanism that involves a highly reactive species, such as the proposed 16-electron iron compounds. The conclusion that the disubstituted product has formed to a large extent already is supported by the finding that the reactions can be run in an extremely short period of time.

Information which was obtained in the attempt to prepare the complex $Fe(CO)_3(AsPPh_3)_2$ is also believed to support the proposed mechanism. The conditions under which the reactions were performed are described under II.3.2. Since the reactions were performed at reflux temperature of 1-butanol and resulted mainly in decomposition of the iron complexes these reaction are of little value. However, a reaction performed under modified conditions (II.3.2.2) is thought to be of greater value. This reaction yielded a mixture of only small amounts of mono- and disubstituted

EXTRACT   (fig. 26)

Minima List:
X=   1580.3   Y=   72.693
X=   1884.2   Y=   61.880
X=   1940.5   Y=   13.472
X=   1971.2   Y=   40.657
X=   2011.6   Y=   84.571
X=   2049.1   Y=   20.881
6 Minima Detected

%TRANSMITTANCE

84.448   70.013   55.577   41.142   26.708   12.271

WAVENUMBERS (CM-1)

2230.0   2126.1   2041.2   1954.4   1867.5   1780.6   1693.7   1606.9   1520.0

100

AsPh3 DERIVATIVES OF IRON PENTACARBONYL   (fig. 27)

Minima List:
X=   1886.5   Y=   67.891
X=   1943.8   Y=   6.4042
X=   1973.8   Y=   42.659
X=   2049.6   Y=   11.270
    4 Minima Detected

%TRANSMITTANCE

WAVENUMBERS (CM-1)

product. Below two spectra are shown which are labeled as "EXTRACT" (fig. 26) and "AsPh$_3$ DERIVATIVES OF IRON PENTA-CARBONYL" (fig. 27). The spectrum obtained from the dichloromethane extract shows the presence of mainly mono-substituted product (2049.1, 1971.2, and 1940.5 cm^{-1}) as well as small amounts of formyl complex (2011.6, 1884.2, and 1580.3 cm^{-1}). The presence of disubstituted product can not be concluded from this spectrum due to the presence of the formyl complex. The second spectrum which was obtained from the dried precipitate after addition of hexane to the dichloromethane extract clearly shows the presence of a small amount of Fe(CO)$_3$(AsPh$_3$)$_2$ (1886.5 cm^{-1}). The result of this experiment is interpreted as a consequence of the nucleophilicity of the triphenylarsine, which is less nucleophilic than phosphine ligands, as well as a result of the electron donor properties of the arsine. Assuming that the proposed mechanism is correct, the out-come of the reactions performed with AsPh$_3$ can be explained by the properties of the ligand. Since triphenylarsine is not as good a nucleophile as phosphine ligands and due to its decreased electron donor ability compared to phosphine ligands the proposed substituted hydrido tricarbonyl com-plex has properties which do not favor a continuation of the reaction. In the arsine intermediate the hydrogen is less hydridic than in the corresponding phosphine inter-mediate. Thus, the proposed compound is less likely to dissociate a hydride, but rather dissociates the arsine

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ligand and causes decomposition of the iron complex. This would explain the formation of only very little amounts of disubstituted product, as well as large amounts of decomposition products, which were apparent by the black color of the residue after evaporation of the solvent. The formation of small amounts of monosubstituted product can be explained by the dissociation of hydride from the tetracarbonylhydridoferrate(0) and subsequent substitution, a side reaction which has been outlined earlier.

Finally, a reaction shall be mentioned which is also believed to support the proposed mechanism. As described under II.2.2.5 the reaction between iron pentacarbonyl and triphenylphosphine was also performed in ethanol. The reaction yielded only 14 % of product after five hours of reflux. This result is interpreted as resulting from the low boiling point of ethanol. Due to the low reflux temperature not enough energy is provided to facilitate the dissociation of CO from the hydridoiron tetracarbonyl complex at a reasonable rate, resulting in a slow formation of the desired product. The steps in the mechanism after the formation of the substituted hydrido species are not influenced by the low boiling point of the solvent.

III.3 Investigation of the Gaseous Side Products

3.1 Analysis of the Composition of the Gas

3.1.1 Infrared Analysis of the Gas

The composition of the gas that formed upon addition
of iron pentacarbonyl to a solution containing sodium boro-
hydride was analysed by infrared spectroscopy. First a
spectrum of 1butanol vapor was taken by evaporating
1-butanol into an evacuated gas cell. In order to obtain
an infrared spectrum of the gas sample an experiment was
performed in which the gas was purged through a flask,
which had been rinsed with nitrogen. When the formation
of gas from the reaction slowed down the flask in which the
gas was collected was sealed. The content of the flask
was then expanded into an evacuated gas cell and the spec-
trum recorded. The spectra obtained are shown below and
are labeled as "BUTYLALCOHOL VAPOR" and "GAS SAMPLE" (fig.
28) respectively. By comparing the two spectra it becomes
obvious that one component of the collected gas is
1-butanol. The next step in identifying the composition of
the collected gas was to subtract the spectrum obtained
from 1-butanol vapor from that of the gas sample. After
the subtraction the spectrum labeled as "SUBTRACTION: GAS
SAMPLE MINUS BUTYLALCOHOL VAPOR" (fig. 29) was obtained.
An expanded part of the spectrum (2300.0 to 1900.0 cm^{-1}) is

BUTYLALCOHOL VAPOR

(fig. 28)

GAS SAMPLE

WAVENUMBERS (CM-1)

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SUBTRACTION: GAS SAMPLE MINUS BUTYLALCOHOL VAPOR (fig. 29)

Minima List:
X= 2014.1   Y= 72.833
X= 2018.4   Y= 81.834
X= 2034.8   Y= 84.505
3 Minima Detected

%TRANSMITTANCE

WAVENUMBERS (CM-1)

ROTATIONAL FINE STRUCTURE OF THE VIBRATION-ROTATION BAND OF CO   (fig. 30)
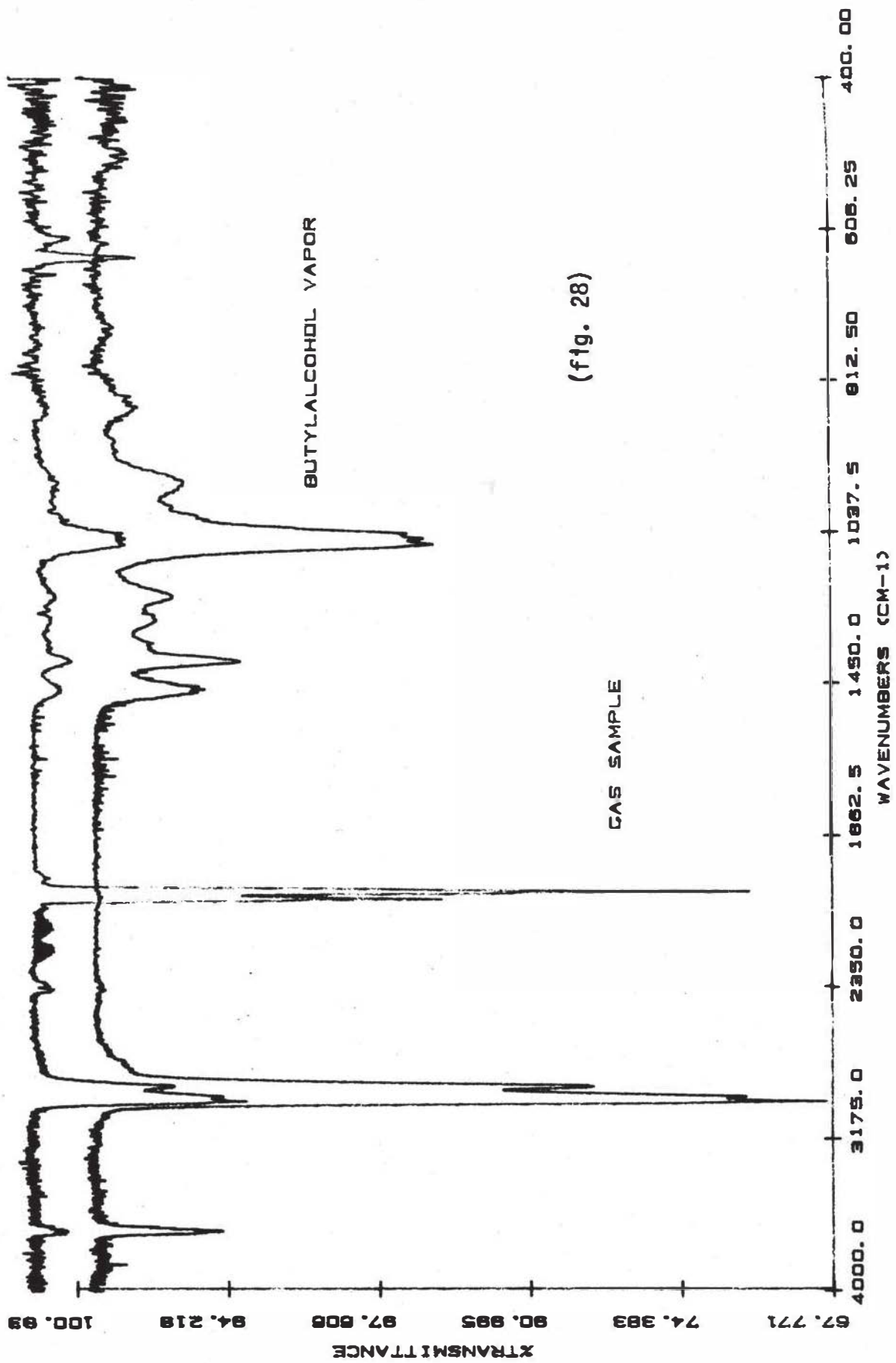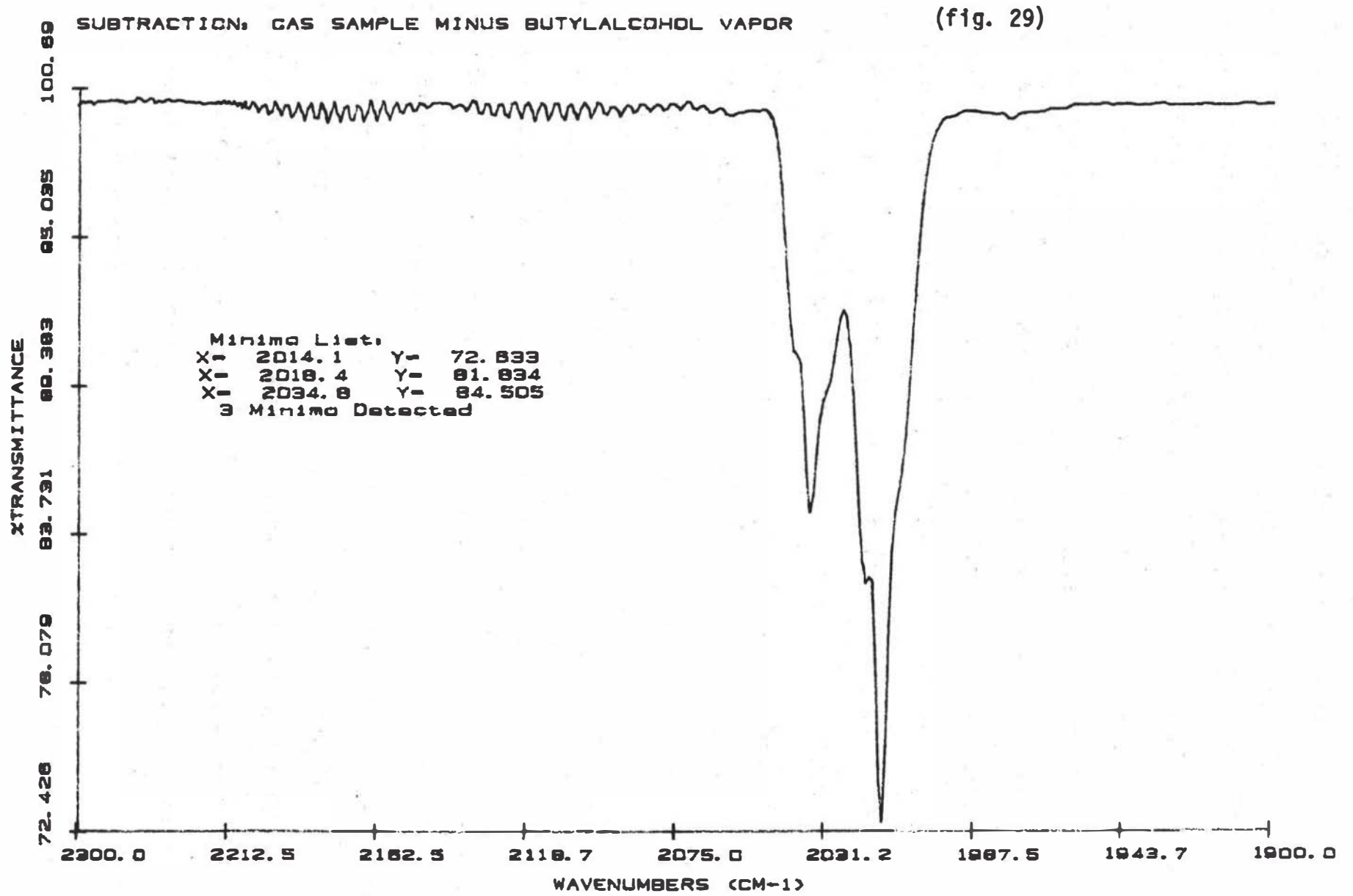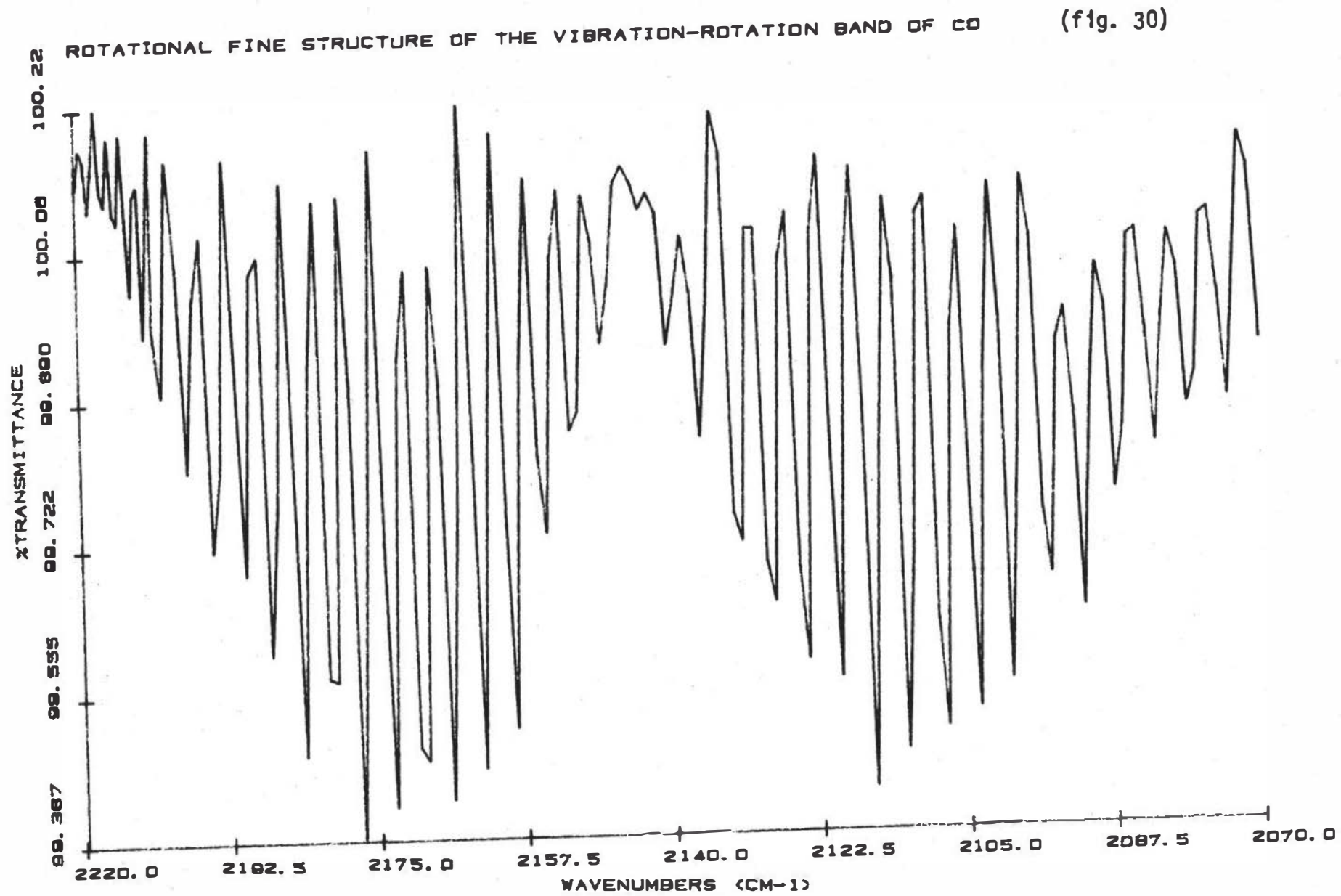
Table III.3.1.1 Wavenumbers of Lines in the $C^{12}O^{16}$ $v = 0 - 1$ Infrared Band

J	R(J) (lit.[46])	R(J) (obs.)	J – J+1	P(J) (lit.[46])	P(J) (obs.)	J – J-1
0	2147.084 cm^{-1}	2147.6 cm^{-1}	0 – 1	–	–	–
1	2150.858	2151.2	1 – 2	2139.427 cm^{-1}	2139.8 cm^{-1}	1 – 0
2	2154.599	2155.0	2 – 3	2135.548	2136.1	2 – 1
3	2158.301	2158.8	3 – 4	2131.633	2132.0	3 – 2
4	2161.971	2162.5	4 – 5	2127.684	2128.1	4 – 3
5	2165.602	2165.9	5 – 6	2123.700	2124.2	5 – 4
6	2169.200	2169.6	6 – 7	2119.681	2120.2	6 – 5
7	2172.759	2173.3	7 – 8	2115.632	2115.9	7 – 6
8	2176.287	2176.6	8 – 9	2111.545	2111.8	8 – 7
9	–	2180.2	9 – 10	–	2107.8	9 – 8
10	–	2183.8	10 – 11	–	2103.8	10 – 9
11	–	2187.0	11 – 12	–	2099.4	11 – 10
12	–	2190.6	12 – 13	–	2095.2	12 – 11
13	–	2193.8	13 – 14	–	2091.2	13 – 12
14	–	2196.9	14 – 15	–	2086.8	14 – 13
15	–	2200.4	15 – 16	–	2082.5	15 – 14

3.1.2 Cooling Experiment

It was rather unlikely that all of the gas consisted
of 1-butanol, iron pentacarbonyl, and carbon monoxide. In
order to obtain more information about the composition of
the gas, a certain volume of a collected gas sample was
expanded into an evacuated container giving a certain pres-
sure. Thereafter, part of the container was cooled with
liquid nitrogen which caused an immediate but small de-
crease in pressure (18 mmHg). This small decrease in
pressure has to be interpreted as caused by the conden-
sation of 1-butanol, iron pentacarbonyl, and carbon mon-
oxide. Since the decrease in pressure upon cooling was
only small the conclusion can be made that the compounds
detected by infrared spectroscopy account only for traces
in the gas mixture, while most of the gas has to be a
compound which does not condense at the temperature of
liquid nitrogen. Thus, the remaining component of the gas
mixture was found to be hydrogen gas, which is infrared
inactive.

3.2 Determination of the Volume of H_2 Formed

The volume of hydrogen gas that formed upon addition
of iron pentacarbonyl to a solution of sodium borohydride
in 1-butanol was determined by collecting the gas in an
inverted graduated cylinder under deionized water. After

the addition of iron pentacarbonyl 700 to 800 mL of hyro-
gen gas formed spontaneously, in less than one minute.
During the following ca. five minutes the volume of hydro-
gen gas increased to approximately 1400 mL, after which the
formation of the gas decreased significantly. A total of
2040 mL of gas was collected at room temperature (23.5 $^{\circ}$C)
before the evolution of the hydrogen gas stopped. The
first 2000 mL of H_2 were collected in a 2000 mL graduated
cylinder. Since the level of water inside and outside the
cylinder were at the same height only corrections for the
temperature, the vapor pressure of water, and the atmosphe-
ric pressure were made. The same corrections were per-
formed for the remaining 40 mL, which were collected in a
1000 mL graduated cylinder, even though the water level
inside and outside the cylinder were at different heights.
The error resulting from this simplification is considered
to be neglectable since 40 mL account for only 2 % of the
total volume. Thus, the correction for the pressure due
to the height of the water column would account for less
than 0.25 % of the total volume (5 mL), which is below the
accuracy of +/- 5 mL of the graduated cylinder used to
determine the volume of the collected gas. Since the
volume of the gas was determined at an atmospheric pressure
of 742 mmHg at 23.5 $^{\circ}$C, the vapor pressure of water, under
which the gas was collected, at that temperature (20 mmHg)
was subtracted to give a pressure of 722 mmHg. Further-
more, the hydrogen gas was assumed to obey the ideal gas

law.   Thus, the volume of the collected gas under standard conditions (760 mmHg, 0 $^{\circ}$C) was calculated as follows:

$$p_0 V_0 = nRT_0 \quad \text{and} \quad p_1 V_1 = nRT_1$$
$$nR = p_0 V_0 / T_0 = p_1 V_1 / T_1$$
$$V_0 = p_1 V_1 T_0 / p_0 T_1$$

where: p_0 = 760 mmHg, T_0 = 273.2 K, p_1 = 722 mmHg,

V_1 = 2040 mL, T_1 = 296.7 K

$$\frac{722 \text{ mmHg} \times 2040 \text{ mL} \times 273.2 \text{ K}}{760 \text{ mmHg} \times 296.7 \text{ K}} = 1780 \text{ mL}$$

This volume accounts for 79.6 mmol of hydrogen gas (22.414 l mol^{-1} under standard conditions).

3.3 Investigation of the Origin of the H_2 Gas

The fact that hydrogen forms if iron pentacarbonyl is added to a solution of sodium borohydride in 1-butanol strongly suggests that the reducing agent is modified. Iron pentacarbonyl or a species that forms after an initial reaction between iron pentacarbonyl and sodium borohydride has to catalyze the formation of hydrogen gas since no obvious reaction occurs in the absence of the iron complex at room temperature. The conclusion that some iron carbonyl complex catalyzes the release of hydrogen gas in 1-butanol is supported by data found in the literature which state that it takes six hours at 60 $^{\circ}$ to release 54 % of the available hydrogen of sodium borohydride in ethanol. Isopropanol and

t-butanol, which are more comparable to 1-butanol than ethanol, do not exhibit a tendency towards the formation of hydrogen by interacting with sodium borohydride.[47] The reaction of sodium borohydride in an alcoholic solvent is a metathesis reaction which occurs stepwise. In the case of 1-butanol the net equations for the different steps can be written as follows:

$$NaBH_4 + ROH \longrightarrow NaOR + BH_3 + H_2 \qquad (A)$$

$$BH_3 + ROH \longrightarrow H_2B(OR) + H_2 \qquad (B)$$

$$H_2B(OR) + ROH \longrightarrow HB(OR)_2 + H_2 \qquad (C)$$

$$HB(OR)_2 + ROH \longrightarrow B(OR)_3 + H_2 \qquad (D)$$

$$B(OR)_3 + NaOR \longrightarrow NaB(OR)_4 \qquad (E)$$

$$R = (CH_2)_3CH_3$$
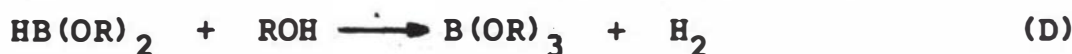
In the attempt to determine the degree of modification of the reducing agent in the reaction with 1-butanol at room temperature the following calculation was done for the reaction of 31.70 mmol of sodium borohydride in 1-butanol in the presence of 7.61 mmol of iron pentacarbonyl which produced 1780 mL (STP) of hydrogen gas. Initially sodium borohydride reacts with iron pentacarbonyl to yield the complex anion $(CO)_4Fe(CHO)^-$ according to equation (F).

$$NaBH_4 + Fe(CO)_5 \longrightarrow Na((CO)_4Fe(CHO)) + BH_3 \qquad (F)$$
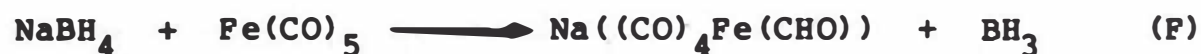
Thus, the initial amounts of reducing agent that can

account for the release of hydrogen gas are 7.61 mmol of BH_3 and (31.70 mmol - 7.61 mmol) = 24.09 mmol of $NaBH_4$ if the above reaction goes to completion. According to equation (A) 24.09 mmol of H_2 and BH_3 are formed, giving a total of 31.7 mmol of BH_3 present in the reaction mixture. The volume of 24.09 mmol of hydrogen gas under standard conditions is 540.0 mL. Further reaction according to equation (B) yields an additional 31.7 mmol of hydrogen gas giving a total volume of 1251 mL of gas. A reaction according to equation (C) would increase the expected volume of collected hydrogen gas to a total of 1962 mL at standard pressure (760 mmHg) and temperature (273.2 K). Comparing the calculated volume of gas with the measured volume of 1780 mL (STP) a deviation of 9.05 % between these two values is calculated. In estimating the accuracy of the experimental result the accuracy of the weight of sodium borohydride was found to have the greatest effect on the amount of collected hydrogen gas. An error of 0.01 g in the determined weight of sodium borohydride results in a deviation of 1 % in the amount of measured hydrogen gas. From the above calculations it can be assumed with reasonable certainty that reactions according to equations (A) through (C) occur in the crude reaction mixture at room temperature in the absence of ligand to give an overall reaction according to equation (G).

$$NaBH_4 \ + \ 3 \ ROH \ \longrightarrow \ NaOR \ + \ HB(OR)_2 \ + \ 3 \ H_2 \qquad (G)$$

The mono-hydrido boron compound is most likely present in solution as its dimer. In calculating the volume of released hydrogen gas it was assumed that all reactions, (A) through (C), go to completion. Considering the possibility that the reactions occur to a slightly lesser extent, would result in a smaller volume of the measured gas as observed.

In order to obtain further evidence for the conversion of the reducing agent the residue after extraction with dichloromethane (compare II.2.2.1) was examined. First, a ^{1}H NMR spectrum of 1-butanol was taken using TMS as an internal standard. The spectrum obtained is shown below as the lower spectrum. The upper spectrum was obtained from the residue dissolved in deuterated chloroform (fig. 31). A single peak which can be seen in this spectrum at 7.3 ppm is due to non-deuterated chloroform. The observed chemical shifts, their assignments, and intensities are listed below. It should be noted that in the spectrum obtained from the residue the peak for the hydroxyl proton at 5.15 ppm is missing. Furthermore, the methylene protons next to the oxygen are shifted by 0.17 ppm downfield due to increased deshielding of these protons caused by the inductive effect of boron bonded to oxygen. From the above observations the tetrabutylborate anion as well as the tributylborate are considered possible structures that would give rise to the observed ^{1}H NMR spectrum.

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(fig. 31)

alkoxyboron compound

$CH_3(CH_2)_3OH$

PPM
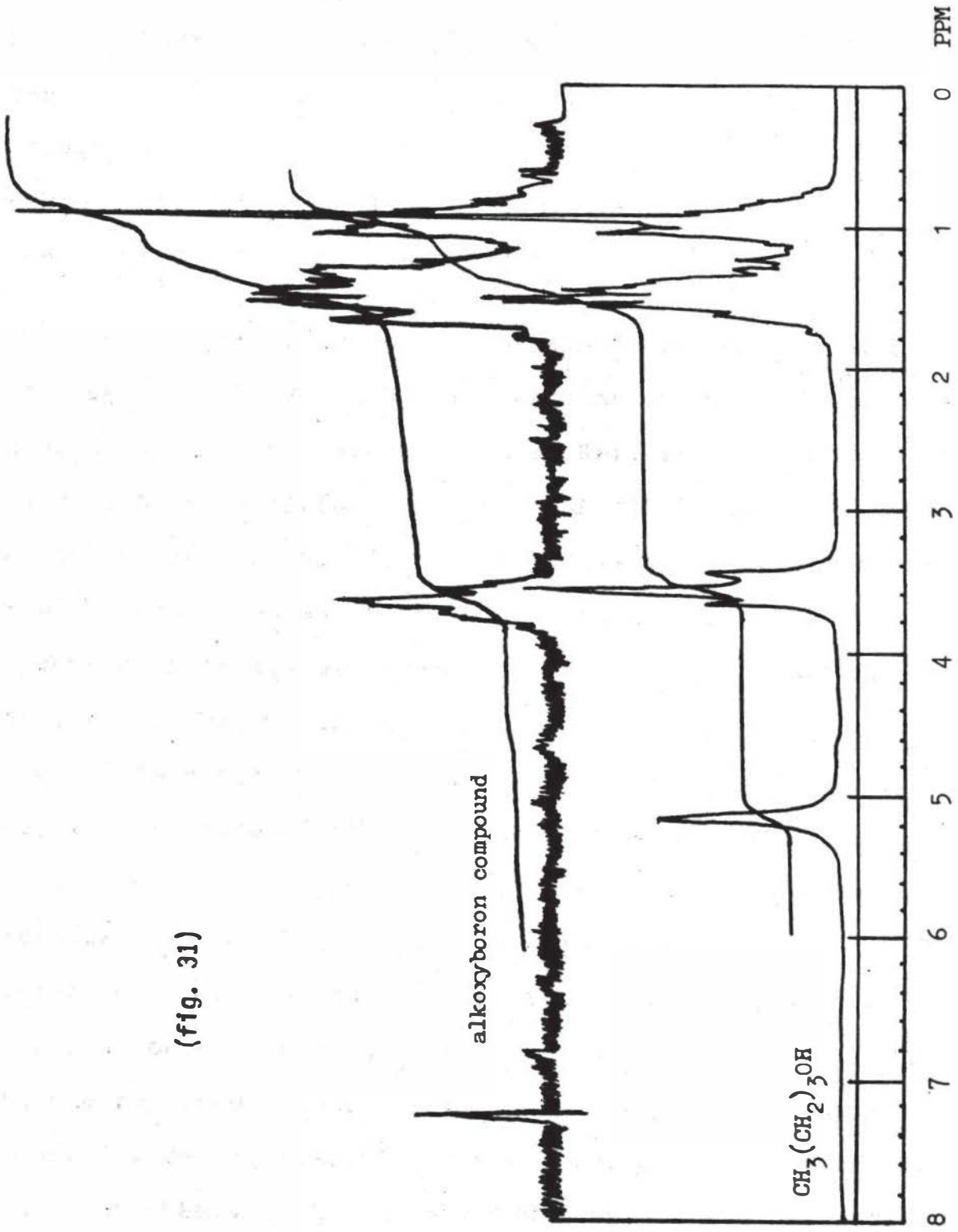
Table III.3.3.1: ^{1}H NMR Data of Butanol and Alkoxyboron
Compound

H	BuOH	B Compound	Intensities
O-H	5.15	-	1 H
O-CH$_2$-	3.55	3.72	2 H
-CH$_2$-	ca. 1.6	ca. 1.6	4 H
-CH$_3$	ca. 1.0	ca. 1.0	3 H

Further evidence for the assigned composition of the residue as well as additional information was obtained from a spectrum of the residue taken in KBr, which is shown below labeled as "RESIDUE FROM EXTRACTION" (fig. 32). The peaks at 2961.0, 2934.1, and 2875.5 wavenumbers are due to C-H stretching modes of the butyl chain, compare with spectrum of 1-butanol vapor. A strong band at 1348.5 cm^{-1} is attributable to the asymmetric stretching frequency of the B-O bond system in a planar alkyl borate.[47] A rather striking feature of the spectrum is the strong absorption in the O-H region. This strong absorption can be due to residual 1-butanol or, which is more likely, due to moisture in the residue. The latter being supported by the observation of a strong peak at 1615.5 cm^{-1}, which is close to the reported frequency of 1595 cm^{-1} for the fundamental bending mode of water.[45] Another possible explanation for the peak observed at 1615.5 wavenumbers is the presence of a compound of the formula $((BuO)_2BH)_2$, which would result from incomplete reaction beween the reducing agent and

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RESIDUE FROM EXTRACTION

(fig. 32)

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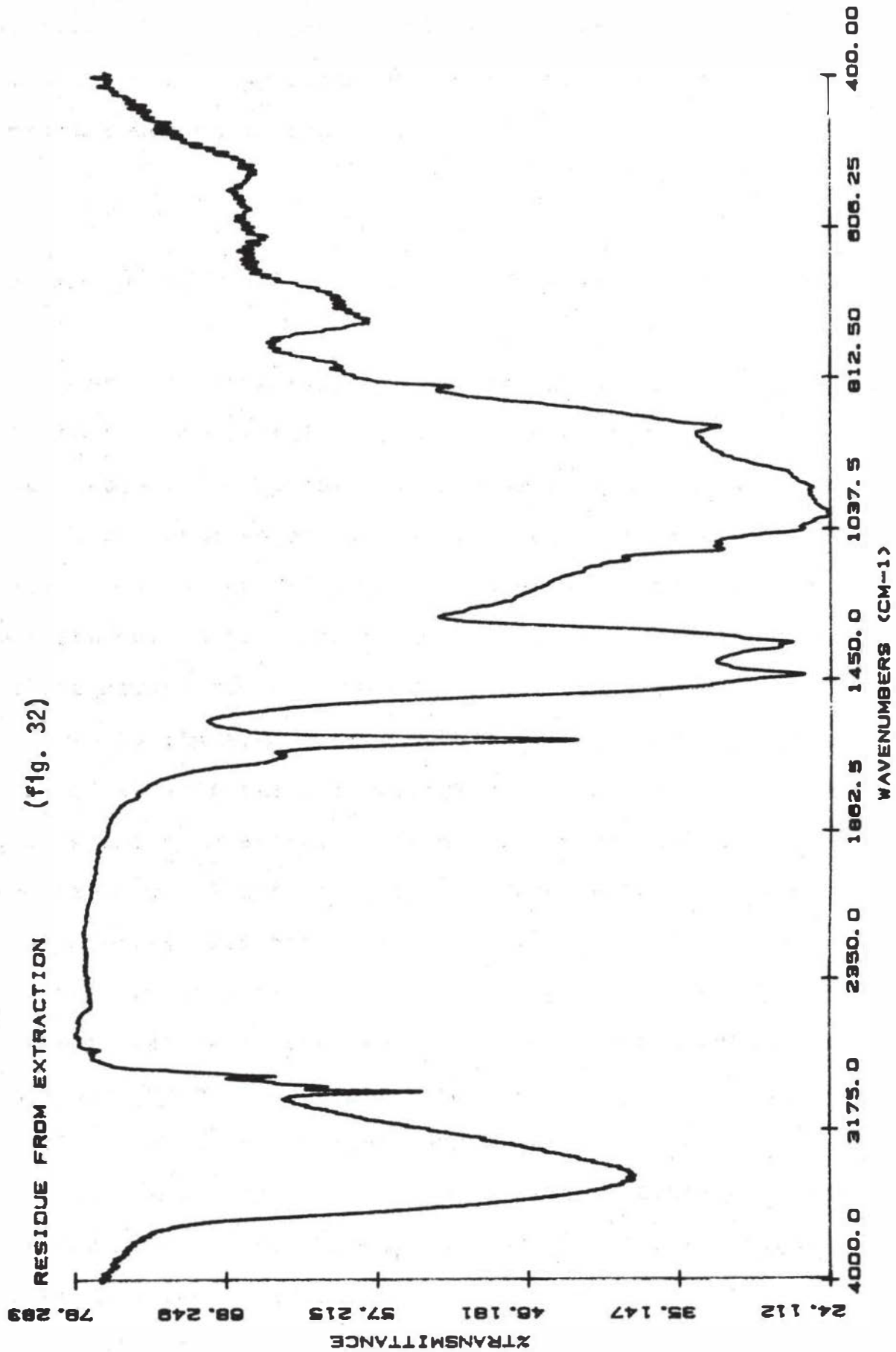
l-butanol. The presence of the above dimer was considered possible after comparison of the spectrum obtained with spectra reported in the literature.[48]

3.4 Conclusion

Since the investigation of the origin of the hydrogen gas and the modification of the reducing agent were not the major goals of the present work, these reactions were not subject to detailed analysis. However, from the work done the following conclusions on the course of the reaction can be drawn, which provide an overview on the reactions of the reducing agent occurring in the crude reaction mixture. Innitially, the sodium borohydride reacts with iron penta-carbonyl to form the tetracarbonylformylferrate(0) anion, which might be the species responsible for the catalysis of the observed release of hydrogen gas from the reaction of sodium borohydride with the alcoholic solvent. At room temperature the modification of the reducing agent proceeds to the formation of the mono-hydrido boron compound, which undergoes further reactions upon heating. After a period of reflux the reducing agent has been converted to a substance which remains as a white residue after extraction with dichloromethane. Spectral analysis of the residue indicated that the residue consists of a mixture of different boron compounds.

III.4 Summary and Conclusion

In the present work it has been shown that phosphine trans-substituted derivatives of iron pentacarbonyl can easily be prepared under reducing conditions in refluxing 1-butanol. In the presented method sodium borohydride was used as the reducing agent and the method has been shown to yield good to very good results for the ligands PPh_3, PPh_2Me, PPh_2CHCH_2, $P(c-C_6H_{11})_3$, $P(n-C_4H_9)_3$, and PPh_2H. The disubstituted product forms under the given conditions after an extremely short period of reflux. In the presence of the reducing agent the starting material $Fe(CO)_5$ is first converted to the corresponding iron formyl complex which undergoes thermally facilitated hydride migration to form the tetracarbonylhydridoferrate(0) anion. This hydrido species is believed to be the reactive intermediate which first undergoes substitution with phosphine ligand and then yields the disubstituted product after hydride loss and further substitution. The reaction was found to proceed with little formation of monosubstituted product.

Due to the sensitivity of the iron pentacarbonyl, the intermediates, and the products to oxygen all reactions had to be performed under an atmosphere of nitrogen. All products have been found to be sensitive to oxygen especially if in solution, with the rate of decomposition depending on the kind of ligand. However, if dry and under vacuum no apparent decomposition takes place over an extended period

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of time.

The value of the presented synthesis is based on its high selectivity, extremely short reaction time, good to very good yields, and its simplicity.

Even though the described synthesis of $Fe(CO)_3(PR_3)_2$ complexes compares favorably with known preparations further work will have to be performed. One point of interest will be to optimize the reaction conditions, especially with respect to the amount of reducing agent used. An academic aspect of further work will be the elucidation of the final steps of the reaction mechanism. The latter is expected to reveal a new reaction pathway for the synthesis of $Fe(CO)_3(PR_3)_2$ complexes via the tetracarbonylhydridoferrate(0) anion.

Addendum

While this thesis was written, further experiments were performed by Dr. R. L. Keiter and Ms. Carol Boecker to elucidate the mechanism of the described reaction. It has been shown that $Fe(CO)_4PPh_3$ can not be converted to the disubstituted iron complex under reducing conditions in the high boiling solvent 1-butanol to a significant extend. Only traces of $Fe(CO)_3(PPh_3)_2$ were observed which are most likely the result of a thermally facilitated reaction. This provides strong evidence that the reaction under investigation does not proceed via the monosubstituted complex. Furthermore, it was shown using triphenylphosphine as the ligand that only one equivalent of sodium borohydride is required in the reaction. The yield obtained from that reaction was in the order of those obtained if a four-fold of the reducing agent was used. The use of less sodium borohydride results in the desirable reduction of alkoxyboron compounds in the reaction mixture, making the work-up easier and reducing the costs of the synthesis.

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Summary of Reported Preparations of $Fe(CO)_3(PR_3)_2$ Complexes

Ref.	Start. Mat.	Equ.	Reaction Conditions	Purification	Products and Yields
4	$Fe(CO)_5$ PPh_3	-	-	-	-
5	$Fe(CO)_5$ PPh_3	1.0 0.91	Carius tube, 3 hrs. at 110 ^{o}C, no solvent	ppt. washed with ether, dis- solved in benzene, filtration, evaporation of solvent, sub- limation of residue	$Fe(CO)_4PPh_3$ $Fe(CO)_3(PPh_3)_2$ no yields given
6	$Fe(CO)_5$ PPh_3	1.0 0.83	refluxing $c-C_6H_{12}$ (b.p. 161.0 ^{o}C) 1 hr. under N_2	crude rxn. mix. diluted with equal vol. of petroleum ether, cooling, filtration, washed with petrol. ether, dried, separation by vac. sublimation	$Fe(CO)_4PPh_3$ 15 % $Fe(CO)_3(PPh_3)_2$ 15 %
6	$Fe(CO)_5$ PPh_3	1.0 0.75	"	"	$Fe(CO)_4PPh_3$ 15 % $Fe(CO)_3(PPh_3)_2$ 15 %

Ref.	Start. Mat.	Equ.	Reaction Conditions	Purification	Products and Yields
6	$Fe_3(CO)_{12}$	1.0	dioxane or THF	cooled, filtered, washed	$Fe(CO)_4PPh_3$ 34 %
7	PPh_3	0.28	ca. 70 $^{\circ}$C	with dioxane or THF, partial	$Fe(CO)_3(PPh_3)_2$ 27 %
			45 min. under N_2	evaporation of solvent, ppt.	
				with MeOH or EtOH, cooled,	
				filtered, washed with petro-	
				leum ether, sublimation, and	
				further separation	
	$Fe_3(CO)_{12}$	1.0	"	"	$Fe(CO)_3(PPh_3)_2$
	PPh_3	exc.			no yield given
8	$Fe_3(CO)_{12}$	1.0	solvent hexane	no purification, kinetic	$Fe_3(CO)_{11}PR_3$
	PPh_3	ca.	stirring under N_2	data obtained by monitoring	$Fe(CO)_4PR_3$
	PBu_3	10	temp.: 25 - 35 $^{\circ}$C	the decrease in absorbance	$Fe(CO)_3(PR_3)_2$
				at 2045 cm^{-1} due to $Fe_3(CO)_{12}$	no yields given

Ref.	Start. Mat.	Equ.	Reaction Conditions	Purification	Products and Yields
10	$Fe(CO)_5$	2.5	irradiation for 12 hrs.	Al_2O_3 column, column eluted	$Fe(CO)_4P(c-C_6H_{11})_3$ 46 %[*]
	$P(c-C_6H_{11})_3$	1.0	in benzene at room	with C_6H_6, evaporation of	$Fe(CO)_3(P(c-C_6H_{11})_3)_2$ 35 %[*]
			temperature	solvent, sublimation of Fe-	
				$(CO)_4PR_3$ under high vacuum,	
				recrystal. of $Fe(CO)_3(PR_3)_2$	
				from heptane	
	$Fe(CO)_5$	10.0	irradiation for 24 hrs.	vacuum destillation, sepa-	$Fe(CO)_4P(C_4H_9)_3$ 64 %[*]
	$P(C_4H_9)_3$	1.0	in heptane at room	ration of product mixture	$Fe(CO)_3(P(C_4H_9)_3)_2$ 13 %[*]
			temperature	by recrystallization from	
				$MeOH/H_2O$ and heptane	
13	$Fe(CO)_5$	1.0	irradiation of reac-	no purification: product	$Fe(CO)_3(PPh_3)_2$ 68 %
	PPh_3	4.8	tants in cyclohexane	ppt. from solution, unre-	$Fe(CO)_3(P(c-C_6H_{11})_3)_2$ 73 %
	$P(c-C_6H_{11})_3$	5.0	in a water cooled ves-	acted start. mat. and mono-	$Fe(CO)_3(P(n-C_4H_9)_3)_2$ 33 %
	$P(n-C_4H_9)_3$	2.8	sel for 6 to 15 hrs.	subst. prod. are sol. in	
				cyclohexane	

[*] Yield was calculated with respect to the amount of ligand used.

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Ref.	Start. Mat.	Equ.	Reaction Conditions	Purification	Products and Yields
15	$Fe(CO)_5$	15	irradiation for 2 hrs. at room temperature under N_2, 150 °C for 1 hr. irradiation for 1 hr. at 150 °C, cooled down to room temp., removal of excess $Fe(CO)_5$	extraction with THF, chromatographed on Al_2O_3 column, eluted with THF, ppt. with H_2O, recrystallization from heptane	$Fe(CO)_4PPh_3$ 85 %[*]
	PPh_3	1.0			$Fe(CO)_4P(n-Bu)_3$ 34 %[*]
					$Fe(CO)_3(P(n-Bu)_3)_2$ 31 %[*]
					$Fe(CO)_4PMe_2Ph$ 70 %[*]
					$Fe(CO)_3(PMe_2Ph)$ 11 %[*]
					Reaction conditions were selected to optimize the yield of $Fe(CO)_4PR_3$
	$P(n-Bu)_3$	1.0	"	elution with pentane, eluant concentrated to dryness, products fractionally distilled in vacuo	
	PMe_2Ph	1.0			

[*] Yield was calculated with respect to the amount of ligand used.

Ref.	Start. Mat.	Equ.	Reaction Conditions	Purification	Products and Yields
16	$Fe(CO)_5$	2.7	20 ml of blue THF (0.1	removal of volotiles under	$Fe(CO)_4PPh_3$ 69 %
	PPh_3	1.0	M in benzophenone)	red. pressure, remaining so-	
	$Fe_2(CO)_8^{2-}$ -		added to PPh_3 and Fe-	lid stirred with 100 ml boi-	
	catalyst		$(CO)_5$, ppt. of Na_2Fe_2-ling heptane until color		
			$(CO)_8 \cdot xTHF$, stirring,	changed, filtration, cryst.,	
			refluxing under N_2 for	crystals rinsed with pentane	
			3 hrs.	dried in vacuo	
	$Fe(CO)_5$	1.8	CH_3CN as solvent,	filtration yellow ppt.,	$Fe(CO)_4PPh_3$ 51 %
	PPh_3	1.0	18 hrs. at room temp.	washed with MeOH and pen-	
	$Fe_3(CO)_{11}^{2-}$	.045	under N_2	tane, dried in the air	
	or				
	$Fe_2(CO)_8^{2-}$	.045			
	$Fe(CO)_5$	2.0	CH_3CN as solvent,	crystallization from	$Fe(CO)_4PPh_3$ 52 %
	PPh_3	1.0	3.5 hrs. of refluxing	boiling heptane	
	$Fe_4(CO)_{13}^{2-}$	.05			

Ref.	Start. Mat.	Equ.	Reaction Conditions	Purification	Products and Yields
16	a. $Fe_3(CO)_{11}^{2-}$	.49	CH_3CN as solvent	filtration • yellow ppt.,	a. $Fe(CO)_3(PPh_3)_2$ 37 %[*]
	b. $Fe_2(CO)_8^{2-}$	?	a) 10 hrs. under N_2 at	washed with CH_3CN and pen-	b. $Fe(CO)_3(PPh_3)_2$ 32 %[*]
	c. $Fe_4(CO)_{13}^{2-}$	.85	room temperature	tane, dried in the air	c. $Fe(CO)_3(PPh_3)_2$ 22 %[*]
	PPh_3		b) 5 days under N_2 at		
			room temperature		
			c) 4 hrs. of refluxing		
17	$Fe(CO)_5$	2.0	ligand and catalyst	removal of catalyst and un-	$Fe(CO)_4PR_3$ 38 to 99 %
	PPh_3		added to 30 ml of	reacted ligand by column	depending on ligand, ca-
	PPh_2Me		toluene, heated to re-	chromatography, evapora-	talyst, and reaction time
	$P(C_6H_{11})_3$		flux, addition of Fe-	tion of solvent and $Fe(CO)_5$	
	$P(n-Bu)_3$	1.0	$(CO)_5$	on a rotary evaporator, re-	
	CoX_2	.030	rxn. time: .5 - 6 hrs.	crystallization from CH_2Cl_2	
	X = Cl, Br,		depending on ligand and	/hexane where necessary	
	or I		catalyst		

[*]Yields are based on 1 $Fe(CO)_3(PPh_3)_2$ per 1 Fe atom.

Ref.	Start. Mat.	Equ.	Reaction Conditions	Purification	Products and Yields
17	$Fe(CO)_4PPh_3$	1.0	starting material added to 10 ml of toluene, reflux for 32 hrs.	column chromatography	$Fe(CO)_3(PPh_3)_2$ 75 %
	PPh_3	1.0			
	$CoCl_2 \cdot 2H_2O$	.10			
	$Fe(CO)_5$	1.0	30 ml methyl ethyl ketone, reflux for 24 hrs.	solvent removal, column chromatography	$Fe(CO)_3(PPh_3)_2$ 53 %
	PPh_3	2.0			
	$CoI_2 \cdot 4H_2O$	.030			
	$Fe(CO)_5$	1.0	"	column chromatography, recrystallization from CH_2Cl_2/ pentane at $-78\ ^{o}C$	$Fe(CO)_3(PPh_2Me)_2$ 57 %
	PPh_2Me	2.0			
	$CoI_2 \cdot 4H_2O$	.030			
21	$Fe(CO)_5$	-	$NaBH_4$-diglyme slurry under N_2, addition of $Fe(CO)_5$ at room temp. - formation of gas (H_2 and CO) red solution	-	no compounds isolated, no compounds positively identified guess: $Fe_3(CO)_{11}^{2-}$ $HFe_3(CO)_{11}^{-}$
	$NaBH_4$				

Ref.	Start. Mat.	Equ.	Reaction Conditions	Purification	Products and Yields
22	$LiAlH_4$	1.0	THF as solvent, stir-	filtration through a short	$Fe(CO)_4PPh_3$ 60 %
	PPh_3	2.5	ring at 25 ^{o}C for 1 hr.	column of alumina, concentra-	ratio mono-/disubstituted in
	$Fe(CO)_5$	3.75	75 ^{o}C oil bath for 50	tion of leuants. (CH_2Cl_2)	crude reaction mixture 10:1
			hrs.	afforded the products, sepa-	
				ration by column chromatogra-	
				phy	
	$LiAlH_4$	1.0	30 mg $LiAlH_4$ + 5.0 mmol	solvent evaporated in open	$Fe(CO)_3(PPh_3)_2$ 71 %
	PPh_3	3.8	PPh_3 in 7 ml THF + 1.5	beaker, extraction of residue	
	$Fe(CO)_5$	1.1	mmol $Fe(CO)_5$, stirred	with THF, precepitation with	
			in 75 ^{o}C oil bath for	H_2O	
			12 hrs., 10 mg $LiAlH_4$		
			added at 12 and 36 hrs.,		
			total rxn. time: 50 hrs.		
	$LiAlH_4$	1.0	$LiAlH_4$ + PPh_3 in 7ml	"	$Fe(CO)_3PPh_3$ 44 %
	PPh_3	2.0	THF + $Fe(CO)_4PPh_3$, 75		
	$Fe(CO)_4PPh_3$	1.0	^{o}C oil bath, 68 hrs.		

Reaction Vessel for the Photochemical Preparation of $Fe(CO)_3(PPh_2C_2H_3)_2$
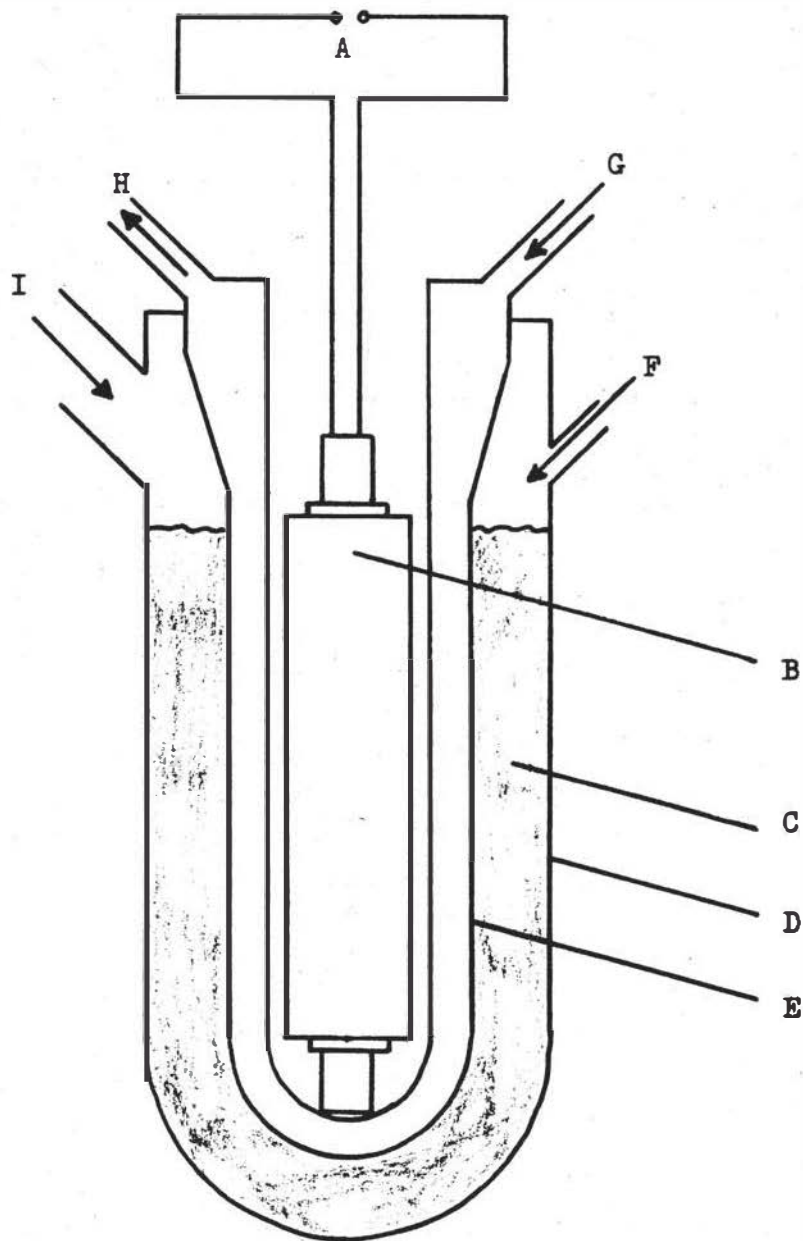
A: 450 Watt transformer

B: 550 Watt Hg arc lamp

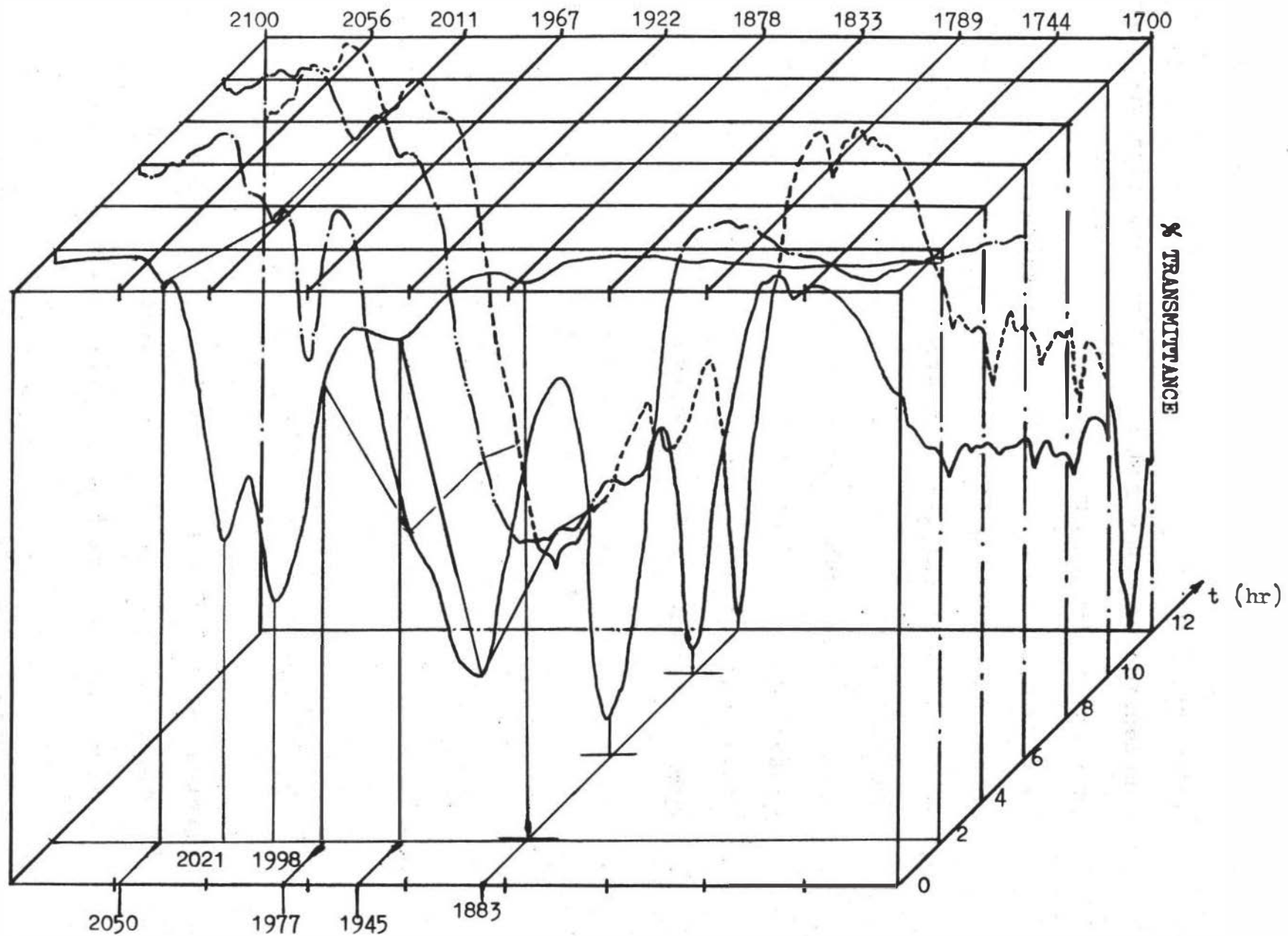C: reaction mixture

D: outer tube

E: inner tube

F: nitrogen inlet

G: inlet for cooling water

H: cooling water outlet

I: filler plug

WAVENUMBERS (cm^{-1})

PHOTOCHEMICAL REACTION OF Fe(CO)$_5$ AND PPh$_2$CHCH$_2$

% TRANSMITTANCE

B-2

t (hr)

DETERMINATION OF INFRARED ACTIVE MODES
OF <u>TRANS</u>-Fe(CO)$_3$(PR$_3$)$_2$ IN THE CARBONYL REGION

Trans diaxial bis(phosphine)tricarbonyliron(0) is of D_{3h} symmetry. The absorptions of these compounds in the infrared spectrum can be determined as follows:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
	4	1	2	4	1	2	*
	3	0	-1	1	-2	1	**
	12	0	-2	4	-2	2	3*
	3	0	-1	1	-2	1	4*
	3	0	-1	-1	2	-1	5*
	6	0	0	4	-2	2	6*

* Number of carbonyl groups which are not shifted by each operation plus one, recorded under the appropriate class.

** Characters corresponding to the particular classes of operations.

3* Reducible representation obtained by multiplying the number of unshifted carbonyl ligands and central atom in each class by the character corresponding to the particular symmetry operation.

4* Subtraction of the assigned translations from the total degree of freedom.

5* Subtraction of the assigned rotations from the total

degree of freedom.

6* Representation of the vibrational modes of the trans
diaxial bis(phosphine)iron tricarbonyl.

The representation of the vibrational modes is a combina-
tion of the irreducible representations A_1', A_2'', and 2 E'
of the D_{3h} symmetry group as concluded from the following
calculation.

$$a(A_2'') = 1/12 \ (6 - 4 + 4 + 6) = 1$$
$$a(A_1') = 1/12 \ (6 + 4 - 4 + 6) = 1$$
$$a(E') \ = 1/12 \ (12 + 8 + 4) \quad = 2$$

After consulting the character table of the D_{3h} group it is
found that the representations A_2'' and E' are bases for x,
y, and z, and hence are infrared active. The represen-
tations A_1' and E' belong to the same representation as
components of the polarizability tensor, and hence are
Raman active.

In order to determine the number of infrared stretching
modes the number of unchanged vectors, pointing from the
metal towards the carbonyl ligands, upon performing of the
particular symmetry operations have to be determined.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
	3	0	1	3	0	1

The representation of the stretching modes is a combination of the irreducible representations A_1' and E' as shown by the following calculation.

$$a(A_1') = 1/12 \; (3 + 3 + 3 + 3) = 1$$
$$a(E') \; = 1/12 \; (6 + 6) \qquad\quad = 1$$

However, only the E' mode is infrared active. By subtraction of the determined stretching modes from the total of vibrational modes one obtains the bending modes A_2'' and E', which are both infrared active.

Thus, the result of the above calculation is that only one stretching mode (E') will be observed in the carbonyl region of the infrared spectrum. The two bending modes A_2'' and E' are both infrared active. These modes are observed below 700 cm^{-1}. The Raman spectrum will show a total of three bands, two of which are due to stretches (A_1', E') and one due to a bending mode (E').